Summary:
This deliverable was produced in the framework of the activities in WP3 related to surface technologies for the CHPM2030 concept. It covers the experimental work carried out in view of demonstrating the technical feasibility of applying electrodeposition at high pressure and high temperature as means to recovery valuable metals from geothermal brines. It contains the design of the lab setup developed by the team at KU Leuven to carry out the proposed study, results of an extensive lab study.

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1 Executive summary

Most geothermal fluids emerge at high temperatures, high pressures, and are rich in base metals (e.g. iron, manganese, zinc, etc.), copper, and silica. Additionally, they also contain traces of noble metals such as silver, gold, and platinum. Currently, most geothermal plants dispose geothermal fluids by means of reinjection to maintain pressure in the reservoir. Therefore, it is of interest to the scientific community to evaluate the potential of various technologies to recover these valuable metals from geothermal brines. This CHPM2030 project ventures to explore the recovery of valuable metals from geothermal fluids. This work package deals with the exploration of the technical feasibility of extraction of the leached metals from the solution phase using electrodeposition at high pressure and high temperature conditions of the brines emerging from the geothermal wellhead. Metals ions present in the leachate can be reduced onto a substrate by passing current to drive the electrode to a potential lower than the reduction potential of the metal. Additionally, the high pressures also prevents silica from precipitating further in the reactor, which can potentially interfere with the metal electrodeposition.

The objective of our work as a part of the CHPM 2030 initiative, the feasibility, performance, and establishing design criteria for trace metal electrodeposition from geothermal brines at elevated temperatures and elevated pressures (ETEP). Based on potential-pH diagrams developed at elevated temperatures and pressures for several metals of interest (Cu, Ag, Ni, Sn, Pb, and Zn), Cu was chosen as the primary metal of interest, based on the reduction potential.

The objectives of the experimental study was to

- Understand the electrochemistry of copper at elevated temperatures and pressures
- Evaluate the effect of various parameters such as temperatures, pressures, Cu$^{2+}$ ion concentration, electrodeposition potential, and deposition times on the recovery of copper.
- Evaluate the effect of silica concentration and Pb$^{2+}$ concentration on the recovery of copper.

Within the scope of evaluating the efficiency, yield, recovery rate, and energy required to recovery copper, the following subtasks were performed

- Understand the role of temperatures and pressures on the solution electrochemical properties.
- Identify properties of geothermal brines to form the basis for synthetic brine preparation.
- Design and construction of a stationary electrode and rotating electrode ETEP batch reactor systems.
- Construction and calibration of a reference electrode that is stable at ETEP conditions.

Mesoporous platinum deposits on a Pt disk, with pore size ranging between 5 nm and 10 nm, was achieved on Pt. The electrodes showed a rapid and stable potential response. Additionally, the stability of the electrode with temperature was confirmed. The mPt quasi-reference electrode was calibrated with the help of Fe(II)/Fe(III) redox couple.
Cyclic voltammograms indicate that the electroreduction of Cu$^{2+}$ ions and subsequent electrooxidation of Cu in aqueous medium at pressures of 50 bar exhibit no significant difference when compared to that at atmospheric pressure. However, SEM images indicate that the electrodeposits at elevated pressures are denser and closely packed. As expected, at temperatures greater than the 373 K and elevated pressures, the cyclic voltammograms exhibited currents that were at least 10 times higher than that obtained at room temperatures. Additionally, the deposit morphology at 373 K does not exhibit a crystalline-type deposit as observed at room temperature, and showed layered deposit which was rather scattered and porous. The porous nature of this deposit can be attributed to the Cu dissolution due to the increased rate of comproportionation reaction at higher temperatures, resulting in the formation of Cu$^+$ ions, which has been shown to be a primary reason behind a uniform conformal coating.

A one factor at a time (OFAT) study was performed to understand the independent impact of temperature, pressure, initial copper concentration, deposition times, and electrodeposition potential on the Faradaic efficiency, yield, recovery rate, and energy required to recover copper was performed. From the study, it can be concluded that the maximum efficiency and minimum energy required to was obtained for both solutions at elevated pressure and solutions at ETEP, indicating that it could be a potential technology that can be used for metal recovery from geothermal fluids. A factorial design or an optimal design of experiments for the major parameters is essential to understand the interaction synergistic or opposing effects of the parameters on the recovery of copper.
2 Introduction

2.1 Relevance of work

The main objective of task 3.1 was to explore the technical feasibility of electrodeposition at elevated temperatures and elevated pressures for the metal recovery from geothermal brines. Geothermal brines - especially originating from an ultra-deep EGS- typically are rich in metal content.

The rationale behind exploring electrodeposition at ETEP to recover metals from geothermal brines are:

- High temperatures are well-known for enhancing the kinetic and mass transport rates of chemical reactions, from Arrhenius theory.
- The high pressures of the geothermal brines allows us to keep them at temperatures high enough without boiling and maintaining the brine in a liquid phase required for metal electrodeposition.
- Electrodeposition is an age-old technique used for a wide variety of metals not limiting to Cu, Ag, Au, Pb, and Cd and it finds applications in a variety of industries including semiconductors, heavy-duty electicals, automobile, corrosion prevention, decorative materials, etc.

Copper is a highly sought metal with a consistently growing demand and is considered one of the key indicators of the world economy.(Gordon, Bertram et al. 2006) The metal possesses excellent properties which finds a wide range of application as wires, heat exchangers to chip manufacturing, anti-microbial touch surfaces, etc. In 2012, the global production of copper from mining was 16.5 million metric ton, the third most mined metal after iron and aluminum in that year.(Lusty and Gunn 2015) The carbon footprint for copper produced from mining via smelting process is estimated to be 2.5 to 8.5 kg CO₂-eq kg⁻¹, by cradle-to-gate life cycle assessment at all sites between 1940 and 2008.(Memary, Giurco et al. 2012) The continued increase in the global demand for the metal and limited availability of economically viable resources makes recovery of such metals a crucial part in the sustainability and achievement of a complete circular economy.

From the composition of leachate solutions obtained from WP 2.4, silica and Pb²⁺ ions were identified as major secondary species that could potentially have an effect on the recovery of copper. The study will then be extended to understand the effect of ETP on the codeposition of copper with other metallic species that are present in geothermal brines.

The experiments were carried out on lab-scale batch reactors designed and developed for the study. In addition to allowing experimentation at smaller scale, the batch reactors allowed for safe handling and personnel safety at high pressures.
2.2 Role of electrochemistry in metal recovery

Electrodeposition as means to recover copper, from a thermodynamic perspective, will also result in the recovery of noble metals such as Pt, Pd, Au, and Ag from the streams, as they reduce and deposit at the cathode at higher potentials. Additionally, depending upon the composition of the waste stream, one can control the electrodeposition potential, thereby allowing for selective recovery and layered deposition which in-turn reduces the number of downstream processes required to increase the metal purity. Several room temperature studies have shown that electrodeposition can be used to recover Cu, Pb, Cd, and As with yields > 98% with final concentrations < 1 ppm. (Friedrich, Ponce-de-León et al. 2004, Reade, Bond et al. 2004, W, H et al. 2004) Several types of electrochemical reactors have been evaluated for effluent treatment and metal recovery not limiting to fluidized bed reactor, (W. Evans, Ding et al. 2005) spouted bed reactor, (Shirvanian and Calo 2005, W. Evans, Ding et al. 2005) porous fixed bed reactor, (Bennion and Newman 1972, Tan, Hasnat et al. 2012) rotating cylinder setup (Nahlé, Reade et al. 1995, Reade, Bond et al. 2004, W, H et al. 2004, Recéndiz, González et al. 2007). Most of these reactors employ a three dimensional electrode to maximize the treatment capacity and metal recovery rates. Pletcher and Walsh have evaluated in detail several types of three dimensional electrodes broadly categorized into stationary electrodes (porous and packed bed type electrodes) and moving electrodes (fluidized bed and moving bed electrodes) for effluent treatment. Off-late, a significant amount of recovery studies have involved the use of reticulated vitreous carbon as the substrate, due to their high surface area. (Nahlé, Reade et al. 1995, Friedrich, Ponce-de-León et al. 2004, Reade, Bond et al. 2004, W, H et al. 2004, Reade, Ponce-de-León et al. 2006, Tan, Hasnat et al. 2012) The RVC electrode has been employed in several configurations viz., porous fixed bed reactor with mesh flow electrodes, electrochemical hydrocyclone reactor, rotating cylinder electrode with RVC or or stainless steel mesh electrodes.

2.3 Electrochemistry at Elevated Temperatures and Elevated Pressures (ETEP)

Electrochemical studies at high pressures date back to 1904, where professor Arthur Noyes and his co-workers evaluated the conductivities and ionization of salts, acids. (Noyes, Melcher et al. 1908) Despite the early beginnings, very few electrochemical studies have been done at high pressures. The complexity, risks associated with experimentation, and its minor effect on electrochemical reactions have shunned researchers from experimenting at high pressures. High pressure experiments have been recognized to provide a deeper insight into electrochemical reactions. To perform electrochemical studies at high pressures and temperatures, it is crucial to understand the physical, chemical, and thermodynamic behavior of the electrolytes at such conditions. Secondly, the effect of pressure and temperature on the thermodynamic and kinetic properties of electrochemical reactions is essential design of the experimental setup to carry out elevated temperature and pressure study. Following this we will look at a few relevant applications where electrochemical studies have been performed at elevated temperature and pressure.

2.3.1 Effects of temperature and pressure on the solvent and electrolyte properties

High pressures permit electrochemical measurements in aqueous electrolytes at higher temperatures by increasing their boiling point. (Campagnol, Van Assche et al. 2013) Water is the solvent in geothermal brines and therefore, it is important to understand the changes in the properties of water with pressure.

**Pressure effect on the physical and chemical properties of water:** Depending upon the influence of pressure, properties of liquids exhibit a linear (if they depend on density, which has a linear relation with pressure) or a quadratic relationship with pressure (if they depend on molecular motion and the density which are in turn dependent on pressure). Figure 2-1, shows the various physical properties for water: density, specific volume, dielectric constant, ionic product, isothermal
compressibility, relative viscosity, and self-diffusion coefficient as a function of pressure, expressed
in MPa, using data from the literature. (Hills 1972) From Figure 2-1, it can be observed that all
properties except for viscosity and self-diffusion coefficient exhibit a linear relationship with
pressure.
From Figure 2-1, it can also be observed that for water the density, specific volume, and dielectric
constant - a factor that is dependent on amount of unionized or polarizable material in a unit
volume, exhibits a linear dependence on pressure. Unlike the dielectric constant for most solvents
such as methanol which does not vary with pressure; the dielectric constant of water varies with
pressure, possibly due to the increase in polarizability of water with pressure. From Figure 2-1B, it
can be observed that the ionization product / dissociation constant ($K_W$) of water increases with
increase in pressure, in accordance to Eqn. 1, obtained using a glass electrode designed for high
pressures. (Hamann 1963)

$$E_P - E_1 = -\frac{RT}{F} \ln \left( \frac{K_W}{K_{W1}} \right)$$

(1)

where, $E_P$ and $E_1$ is the emf of the high-pressure glass electrode [V] at pressure P and 1 atmosphere,
respectively; $(K_W)_P$ and $(K_W)_1$ are dissociation constants for water at pressure P and 1 atmosphere,
respectively. Figure 2-1D, shows the pressure and temperature dependence of absolute viscosity
of water, which shows a quadratic dependence on pressure. The ionic conductivity of pure water
increases from 0.7 to 1.0 x 10^{-6} \Omega^{-1}.m^{-1} by a factor of 16 when compressed from 1 bar to 10 kbar at
25 °C. (Giovanelli, Lawrence et al. 2004) This increase in ionic conductivity with pressure is explained
by its dependence on dissociation constant, which is shown to increase significantly with
pressure. (Hills)

![Figure 2-1. Effect of pressure on behavior of various physical properties of water. (A) Density, specific
volume, and dielectric constant. (B) Ionic product and isothermal compressibility (C) Relative viscosity and
self-diffusion coefficient. Data was adopted from Hills. (Hills 1972) (D) Absolute viscosity. (Bett and Cappi
1965)](image)
TEMPERATURE EFFECT ON THE PHYSICAL AND CHEMICAL PROPERTIES OF WATER: The dissociation constant of water is reported to increase rapidly with temperature up to 100 °C, followed by a slow increase reaching a maximum over 5000 times that at 25 °C, further increase in temperatures results in the decrease of the ionic product. The increase in the ionization of water with increasing temperatures, accompanied by the marked decrease in the ionization of the electrolyte is responsible for the hydrolysis of the electrolyte at high temperatures. (Franklin 1908, Noyes, Melcher et al. 1908)

2.3.2 ETEP EFFECTS ON ELECTROLYTES / SOLUTIONS

Solution properties such as equivalent ionic conductivity, ionization product, and mobility play a major role in the field of electrochemistry, and their dependence on pressure and temperature is one that is important to understand. The major effects of temperature and pressure on electrolyte properties is presented in detail below.

PRESSURE EFFECT ON ELECTROLYTE PROPERTIES: The dissociation constant (K) for an electrolyte increases with pressure and is given by the equation below

\[ RT \left( \frac{\partial \ln K}{\partial P} \right)_T = -\Delta \tilde{V}^0 \]

where \( \Delta \tilde{V}^0 \) is the change in standard partial molar volume [m⁴ mol⁻¹] due to dissociation which is defined as follows

\[ -\Delta \tilde{V}^0 = \tilde{V}_{i^0} - \sum_j \tilde{V}_{j^0} \]

where, \( \tilde{V}_{i^0} \) is the standard partial molar volume of the undissociated molecule [m⁴ mol⁻¹], and \( \sum_j \tilde{V}_{j^0} \) is the sum of all the standard partial molar volumes of the dissociated ionic species.

The effect of increasing pressure on the equivalent ionic conductivity (\( \Lambda \)) is shown in Figure 2-2A and 2-2B. (Hills 1972) From Figure 2-2A it can be observed with increasing pressure, the ionic conductance is shown to decrease or quickly upon reaching the maximum, except for H⁺ ions where a constant increase in conductance is observed up to 1000 bar. (Hills) This behavior can be explained by its dependence on the degree of dissociation and the mobility of the ions in [m² V⁻¹ s⁻¹], expressed by (Bard and Faulkner 2001)

\[ \Lambda = z_+ F \mu_+ + z_- F \mu_- \]

where \( z_+ \) and \( z_- \) are the charges on the cation and anion, \( \mu \) is the ionic mobility [m² V⁻¹ s⁻¹] of the ion given by the expression below (Bard and Faulkner 2001)

\[ \mu = \frac{z_i e}{6 \pi \eta r} \]

where \( e \) is the charge on the electron [C]; \( r \) is the hydrodynamic radius of the ion [m]; \( \eta \) is the absolute viscosity of the solution [Pa s]. The initial increase in equivalent ionic conductivity with pressure is due to the increase in degree of dissociation explained by Eqn. 3. Subsequently, at higher pressures, the viscosity increases causing a significant drop in the ionic mobility, thereby decreasing the ionic conductivity. It can also be observed from Figure 2-2A and 2-2B that the ionic conductance variation with pressure is affected with size of ions and the concentration (i.e., higher ionic conductivities are displayed by smaller ions and dilute solutions). Concentrated solutions exhibit a higher drop in conductivity with increasing pressure. The larger drop in conductivity for concentrated solutions is explained by the unavailability of free water (i.e. water that is not associated with the electrostatic field of the ions in the solution) and therefore a lower mobility of
the electrolyte. The **solubility** of an electrolyte increases with pressure, which is given by Eqn. 5.\(^{(1)}\)

\[
RT \ln \frac{S_p}{S_1} = -P \bar{V}_i
\]

where \(S_p\) is the solubility or saturation molality \([\text{mol kg}^{-1}]\) at the pressure \(P\) [Pa], \(S_1\) is the solubility \([\text{mol kg}^{-1}]\) at 1 atm, \(\bar{V}_i\) is the partial molal volume \([\text{m}^3]\) of species averaged over the pressure range \(P\).\(^{(1)}\)

On the other hand, the variation of the solubility of a gas with pressure is given by Henry’s law expressed by the following equation:

\[
S_i = H^{CP} P_i
\]

where, \(S_i\) is the solubility of species in liquid in molarity \([\text{mol m}^{-3}]\), \(P_i\) is the partial pressure of species in gas phase in [Pa], and \(H^{CP}\) is the Henry’s law solubility constant expressed by \([\text{mol m}^{-3} \text{ Pa}^{-1}]\).

**Temperature effect on electrolytes**: Experimental values indicate that, unlike with pressure, the **dissociation constant** for both strong and weak electrolytes decreases with temperature. Ionic conductivity of a solution increases with temperature before reaching a maximum, from which it starts to decrease steadily.\(^{(1)}\) This behavior can be explained by its dependence on the ionic mobility, which increases drastically with temperature, and dissociation constant of the electrolyte, which decreases with temperature. Upon reaching the maximum, the drop in the ionization of the electrolyte tends to dominate the behavior of the electrolyte, thus explaining the drop in ionic conductivity.\(^{(1)}\)

The presence of more than one electrolyte in equilibrium, as observed in geothermal fluids, complicates the behavior of the solution and therefore the estimation of physical and chemical properties at higher pressures. In such a case, semi-empirical models are required to understand the solubility. A recent study provides useful correlations for estimating the thermophysical properties sea water as functions of temperature, salinity, and pressures up to 120 bar.\(^{(2)}\) McKibben et al., carried out well controlled sampling and experimental analyses of geothermal fluids to estimate the metals content in scales and brines.\(^{(3)}\) Based on the metal content in the scales, the authors developed transport models and geochemistries for Au and platinum group elements (PGE). However, the significantly low PGE content in scales, prediction of their mineral state in geothermal fluid composition has proven to be elusive. Therefore we will approach our problem by using concentration ranges reported in literature as a baseline for our study and arrive at a limiting concentration where recovery will no longer be economically possible.\(^{(4)}\)

\[\text{Figure 2-2. Variation of ionic conductance with pressure for (A) different types and (B) Concentration of Electrolyte. (C) Structured Model of Aqueous Solution.} \text{(Hills 1972)}\]
2.3.3 THERMODYNAMICS OF ELECTROCHEMICAL REACTION AT ETP

In 1922, Lewis and Randall, based on their study of the reversible hydrogen electrode, showed that the effect of pressure on the equilibrium potential can be expressed by Equation 7,(Lewis and Randall 1914)

\[ E_2 - E_1 = \frac{RT}{2F} \ln \left( \frac{P_2}{P_1} \right) \]  

(7)

where, \( T \) is the temperature [K], \( E_1 \) and \( E_2 \) are the equilibrium potentials expressed [V] at pressures \( P_1 \) and \( P_2 \), respectively. \( R \) is the gas constant taken as 8.314 J mol\(^{-1}\) K\(^{-1}\), \( F \) is the Faraday constant, 96,485 C mol\(^{-1}\). However, their study was limited to measurements at pressures up to 1.5 bar. Following this, Hainsworth expanded the equilibrium potential measurements for the hydrogen electrode for pressures up to 1000 bar and concluded that Eqn. 1 is able to predict equilibrium potentials within 0.2 mV for pressures up to 300 atmospheres, beyond which the fugacity of hydrogen changes in H\(^+\) ion activity due to dissolution of H\(_2\), need to be taken into account. (Hainsworth and MacInnes 1922, Hainsworth, Rowley et al. 1924) In 1992, Sachinidis et al., investigated the effect of pressure on the behavior of ferri/ferro redox couple where they quantified the changes in molar volumes with pressures according to the expression in Eqn. 8.(Sachinidis, Shalders et al. 1992)

\[ \Delta V^0 = \left( \frac{\partial (\Delta G^0)}{\partial P} \right)_T = -nF \left( \frac{\partial E_0^0}{\partial P} \right)_T \]  

(8)

where, \( \Delta V^0 \) is the standard volume of reaction [mol dm\(^{-3}\)] i.e., difference between the standard partial molar volumes of products and reactants, \( P \) is the pressure [Pa], \( \Delta G^0 \) is the change in Gibbs free energy of the reaction [J mol\(^{-1}\)], \( \partial E_0^0 \) is the formal or equilibrium potential [V], and \( n \) is the number of electrons in the reaction. From Eqn. 8, one can gain insight into the reaction from the knowledge of the variation in formal potential with pressure or the standard volume of reaction.

For example, when the \( \left( \frac{\partial E_0^0}{\partial P} \right)_T \) is positive or \( \Delta V^0 \) is negative i.e., the standard molar volume of the products is lower than that of the reactants, the redox reaction is spontaneous and vice versa.(Cruanes, Drickamer et al. 1992, Cruanes, Drickamer et al. 1995) Additionally, their studies revealed that the effect of pressure is reversible and that an increase in the pressure of 1000 bar resulted in a negative shift of approximately 50 mV for the redox equilibrium or formal potential. However, the shift in peak potential was limited to 16 mV for the same pressure increase.

In summary, the effect of pressure on the equilibrium potential for a redox reaction is manifested in the Nernst equation via changes in the partial pressure and activity in terms of reactants and products. For electrochemical systems with gaseous reactants or products, high pressure offers change in equilibrium potential as expressed by Eqn. 9.

\[ E_{r,P} = E_{r,1\text{ bar}} - \frac{RT}{2F} \ln \prod_{i=1}^{N_g} [(x_i P)^{\Delta N_i}] \]  

(9)

where, \( E_{r,P} \) and \( E_{r,1\text{ bar}} \) is the reversible cell potential at pressure \( P \) and 1 bar, respectively; \( x_i \) is the mole fraction of species \( i \); \( \Delta N_i \) is the difference in the moles of species \( i \) between the reactants and products. As for electrochemical reactions where the reactants or products are present in their condensed state, i.e. aqueous solution and solid state, are incompressible. Therefore, higher pressures pressure has little to no effect on their activity and in turn the equilibrium potential.

The effects of pressure on the kinetics of electrochemical reactions are few and far between. A study, by Ewald and Lim(Ewald and Lim 1957), showed that the diffusion current \( i_d \) for the reduction
of Cu²⁺ ions to Cu⁺ ion decreased linearly with increasing pressure. The diffusion current is given by Eqn. 10.

\[ i_d = \frac{nFADC}{\delta} \]  

(10)

where \( i_d \) is the steady state current [A], \( n \) is the number of electrons in the electrochemical reaction, \( A \) is the area of the electrode [m²], \( C \) is the concentration of the solution [mol m⁻³], \( D \) is the diffusion coefficient [m² s⁻¹] of the reacting species, and \( \delta \) is the diffusion layer thickness [m]. By using the relation expressed in Equation 4, the authors were able to quantify the decrease in diffusion layer thickness at higher pressures by estimating the corresponding increase in concentrations (10% for an increase of 3000 atm, estimated from volume changes) and decrease in diffusion coefficient (23% for an increase of 3000 atm, estimated from changes in viscosity). (Ewald and Lim 1957) The thermodynamics and kinetics of electrode processes using reactant-solvent interactions have been derived from studying the effect of pressure on redox reactions with transition metal complexes.

The variation in the redox potential with pressure has been attributed to the effect of the charge on the metal center on the overall size of the complex and their ability to interact with the solvent. (Cruanes, Drickamer et al. 1992)

2.4 Geothermal brine properties and composition

Geothermal fluids are typically brines at high temperatures and pressures that arise from reservoirs at about 500 m to 3000 m deep. (Hardardóttir, Hannington et al. 2013) Their chemical composition is determined by the geology, minerology, and geochemistry which can be factored into the source rock type, reactivity, depth, reservoir process, temperature and pressure. (Gallup 1998, Bourcier, Lin et al. 2003) The metal content of geothermal brines have been shown to be related to the amount of silica present, i.e. geothermal brines with low silica concentration is consistent with high metal content and high salinity. For example, geothermal fluids at Salton Sea in California are low in silica content ranging from 440 - 540 ppm, and are in-turn high in metal (Zn, Fe, As, and Pb) content and salinity. Alternatively, geothermal brines with high silica concentrations causes the brines to have low metal and salt concentrations. This is in agreement with solubility estimates from empirical data observed in the geothermal fluids from Wairakei, New Zealand which exhibit a large quantity of superior amorphous silica and low salinity and metal content. (Harper, Thain et al. 1992)

The geothermal brine temperatures, silica, and metal content increase with reservoir temperature, thereby providing the motivation for facilities to drill deep wells. Another important factor that determines the composition of geothermal brines is its location and proximity to oceans, active volcanoes, or inactive and extinct volcanoes. The brines obtained from geothermal wells that are in proximity to an active volcano, such as the Reykjanes facility, exhibit no precious metal content. (Kristjánsson 1992, Hardardóttir, Hannington et al. 2013) On the other hand, the brines from wells located in near an inactive or extinct volcano (Wairakei, New Zealand)(Harper, Thain et al. 1992) have a low precious metal content, usually in the ppb range. Wells that are located closer to the ocean cause the brines to be highly saline as observed from the Reykjanes brines. (Kristjánsson 1992) Additionally, the Reykjanes brine have surface temperatures as high as 252 °C at 40 bar at the well head, following the trend that higher temperatures are retained by brines from deeper wells. (Kristjánsson 1992, Hardardóttir, Hannington et al. 2013)

The composition of geothermal brines across several facilities in Europe are reported in the Table 1-1. From literature it can be observed that, although there is a high variability in composition of precious and base metals for samples from the same field there is agreement in the chemical properties, silica content, and salinity. (McKibben, Williams et al. 1990) This could be either due to variation in the brine composition over time, the choice of sampling location and analyses technique.
adopted by different researchers. The understanding of the source for variation is crucial to developing an appropriate technology for metal recovery. As far as sampling location, the brine samples taken at the depth of the geothermal well represent the maximum metal content that can be expected from the well, provided scaling is avoided as they progress up to the surface. On the contrary, the sample taken at the surface does not account for the components that were precipitated as scales in the process equipment and along the length of the pipes. (McKibben, Williams et al. 1990) The chemical nature of precipitates varies by location such as that observed at the flash point, well head, downstream of pressure relief equipment, etc in a similar manner at both Salton Sea (McKibben, Williams et al. 1990) and Reykjanes geothermal fields. (Hardardóttir, Hannington et al. 2013)
Table 1. Properties and composition of brines observed in geothermal over the world. (Karabelas, Andritsos et al. 1989, Gallup 1998, Sanjuan, Millot et al. 2010, Hardardóttir, Hannington et al. 2013)
The selection of the technique for analyses of brine samples dictates the detection limit for a metal species and interference from other metal species present in the samples, have been reported to be the source of some variability in metal concentration measurements. ICP-MS has been shown to...
be accurate for precious metal estimation up to concentrations in the parts per trillion. (McKibben, Williams et al. 1990) Various brine composition and properties obtained from geothermal wells across the world are reported in Tables 1 and 2, and it presents an idea of the variability in the nature of geothermal brines.

2.4.1 EXISTING TECHNOLOGIES FOR METAL RECOVERY FROM BRINES

Metals present in geothermal fluids can either be extracted directly from brines or from residual sludge and scales as they deposit. Acid leaching and biochemical leaching are the major separation techniques used to remove metals from residues. On the other hand, adsorption using ion-exchange resins with solvent extraction and precipitation with hydroxide or H₂S addition is predominantly used to separate metals from brines.

**Silica:** The separation technologies existing today that have been used for silica removal from geothermal fluids are agglomeration, facilitated by polymerization with Mg salts or synthetic polymers or precipitation by increasing pH, cooling, and addition of seed crystals, followed by either ultrafiltration, clarification or centrifugation. At Mammoth lake geothermal plant in California, USA, reverse osmosis was initially used to increase the silica content in brines from 250 ppm to desired level (600 – 700 ppm) in order to facilitate removal using subsequent agglomeration and ultrafiltration steps. (Maimoni 1982)

**Base Metals:** Laboratory studies have shown that Co, Zn, Mn, and Li can be extracted from solution using co-precipitation with aluminum, adsorption with synthetic ion-exchange resins or biological process. However, these processes have not been scaled to commercial levels. On the other hand, Li is extracted from saline brines, at Searles Lake in California, by direct precipitation as dilithium sodium phosphate. Zn is extracted at Salton Sea geothermal plant using a solvent extraction process. (Bourcier, Lin et al. 2003)

Gallup has successfully demonstrated that electrodeposition could be used to extract base metals from geothermal fluids. In the study, electrodeposition was carried out downstream of the clarifier tank, after the removal of the precipitated silica and solids. However, the location of the electrolytic cell in the geothermal process raises concern to losses in metals that precipitated along with silica upon loss of pressure during the flash separation stage. Additionally, the lack of sufficient copper concentration in the brine, piques interest on the achievable copper recovery rate relative to other base metals had it been present in a higher concentration. (Gallup 1993)

**Noble Metals:** Precious metals such as Cu, Pt, Au, and Ag are reported to be present in scales deposited in the pipe-walls as opposed to being present the geothermal fluid. This could be attributed to the drop in geothermal fluid pressure causing the precious metals to precipitate as scales. Precious metals with bisulfide complexes in brines are destabilized by (1) boiling, (2) metal sulfide precipitation, (3) oxidation, and (4) simultaneous decrease in pH. On the contrary, precious metal chloride complexes are removed by (1) reducing temperature, (2) dilution, (3) reduction, and (4) increasing pH. (Bourcier, Lin et al. 2003) Pilot studies, have shown that cementation, which involves the electroless precipitation of a metal by substitution with a less noble metal, have been used to extract noble metals such as Au, Ag, etc. (Maimoni 1982)

2.5 DESIGN CRITERIA & BASIS OF STUDY:

**A basis for the current study was established** from deliverable 1.1. and 1.2, the properties of geothermal fluids that are key to electrochemical metal recovery are listed in Table 3. Based on WP 2, the most promising composition of silica and major electroactive metals Cu, Pb in geothermal rocks samples and from various
geothermal wells across is shown in Figure 2-3. The composition of Cu, Pb, and SiO₂ present in leachates obtained from high pressure leaching experiments conducted are shown in Figure 2-4.

### Geothermal fluid properties (at well-head)

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (mg/l)</td>
<td>10 - 25</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 – 7.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>100 – 250</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>20 - 40</td>
</tr>
<tr>
<td>Flows (l/s)</td>
<td>55 - 350</td>
</tr>
<tr>
<td>Silica content (mg/l)</td>
<td>0.7 – 74%*</td>
</tr>
</tbody>
</table>

*Table 3. Properties of geothermal fluids used as basis for this study.*

#### Figure 2-3. Composition of Cu, Pb, and SiO₂ in rock samples obtained from various geothermal wells across Europe. The Ore types for the rocks are mentioned at the top.

#### Figure 2-4. A short list of leaching conditions (acid concentration and temperature of leaching solutions) that exhibited a promising concentration of Cu, Pb, and SiO₂ in leachates. Obtained from Deliverable 2.1.
2.6 EXPERIMENTAL SETUP FOR KINETIC AND TRANSPORT STUDIES AT ETP

Approaches to pressurize a cell depends upon the choice of (a) a batch setup where in the electrolyte in the reactor is pressurized by reducing the volume of the reactor with a piston or increasing the volume of gas by using a compressor or a high-pressure gas cylinder, (b) a continuous setup where the electrolyte can be supplied to the reactor at a high pressure by means of a pump working in tandem with a pressure regulator. Giovanelli et al., gives an extensive review of the various high-pressure setups used for electrochemical measurements prior to 2004, although they pertain to stationary electrodes alone. (Giovanelli, Lawrence et al. 2004) Four different ETEP reactors with rotating electrode capability has been reported in literature, the schematic diagram for each of these reactors are shown in Figure 2-5. For evaluating the electrochemical kinetic and transport properties, where reactants or products are either in their gaseous phase or some heavy metal ion, one resorts to the use of a rotating electrode (e.g. Rotating disk electrode (RDE), rotating cylinder electrode (RCE), etc.) to establish a control over the diffusion layer thickness and in-turn maintain a steady transport of reacting species to the electrode surface.

Recent studies in high pressure electrochemistry provides a versatile design and robust construction for a ETP electrochemical test station. (Chatzichristodoulou, Allebrod et al. 2013, Wiberg, Fleige et al. 2014, Fleige, Wiberg et al. 2015) Until now, there have been only three studies that utilize a rotating disk electrode at high pressures. (Wiberg, Fleige et al. 2014, Fleige, Wiberg et al. 2015) One of the first, high pressure reactors capable of performing rotating disk electrode studies was developed for fuel cell studies at Brookhaven National Laboratories, where the authors report achieving conditions up to 205 °C and 7.7 bar by using a water-cooled fluorocarbon based magnetic fluid to achieve a hermetic rotating seal. (Mcbreen, Ogrady et al. 1984) In 2006, Lazaro and Jeffrey, used a PTFE lined titanium autoclave with a RDE, for high pressure acid leaching studies of chalcopyrites. (Lazaro and Jeffrey 2006) The sealing of the reactor was achieved using two spring loaded rotating seals and a Viton o-ring. The rotating seals required lubrication and cooling. Recently, Fleige et al., (Fleige, Wiberg et al. 2015, Fleige, Wiberg et al. 2017) developed a high pressure RDE system with a fixed seal capable of holding a pressure of 101 bar, where rotation was achieved by magnetic coupling, rotated from the outside. The study employs a RDE made from glassy carbon or Pt disk sealed in PEEK and a silver quasi-reference electrode. High temperature and high pressure rotating disk electrodes have also been used in corrosion studies. (Papavinasam and R. W. Revie 1998)

In this study, we report the development of a high pressure RDE system with a fixed seal and magnetic coupling to drive the rotation of the electrode. Many similarities exist between this type of setup and the one reported in literature. However, the differences between our system and the one developed earlier, lie in the choice of material, the placement of the pressure regulator, and the option to perform collection or shielding studies using a rotating-ring disk electrode.
Figure 2-5. High pressure rotating disk electrode setup from literature developed by (A) Brookhaven National Laboratory with a maximum temperature of 205 °C and 7.7 bar. (McBreen, Ogrady et al. 1984) (B) P&ID and crossection of HTP setup by Lazaro and Jefferey (Lazaro and Jeffrey 2006) and (C) Detailed drawings of HTP reactor by University of Copenhagen with a design pressure of 200 bar and 200 °C. (Fleige, Wiberg et al. 2015)
2.7 **REFERENCE ELECTRODE AND POTENTIAL MEASUREMENT AT ETEP CONDITIONS**

Pressure and temperature affects the concentrations and viscosity of the redox species in solution by changing the partial molar volume, which depends on how both electroactive and electrochemically inactive species behave under pressure. (Noyes and Coolidge 1903, Noyes 1904, Noyes 1907, Hills 1972) This in-turn results in changes in ionic conductivity and the activity coefficients of redox species, thereby affecting their redox potential. (Noyes and Coolidge 1903, Noyes 1904, Noyes 1907) On the other hand, changes in temperature directly affects the equilibrium potential for redox reaction as explained by the Nernst equation. Therefore, in order to make accurate measurement of potentials at elevated temperatures and pressures requires a reference electrode whose chemistry and potential are well-known at operating conditions. Potential measurements made at high temperatures and pressures make most sense when reported versus the potential of the reference electrode at the temperature and pressure corresponding to that of the working electrode. (Bogaerts 2016) In addition to being reversible, one would desire for the potential of a reference electrode to be stable at working temperatures and pressures. (Macdonald, Scott et al. 1979)

The stability of a traditional reference electrodes at high temperatures and high pressures has been a challenge, as they are prone to undergo thermal hydrolysis at elevated temperatures. Macdonald offers an extensive review and evaluation of high temperature reference electrodes that have been used prior to 1978. (Macdonald, Scott et al. 1979) A list of reference electrodes used at high pressures is presented in Table 4. From Table 4, it is observed that silver-silver chloride (Ag/AgCl) reference electrodes have been predominantly used for high-temperature and high-pressure systems, as they have shown stable redox potentials at these conditions. However, the presence of chlorides is known to cause pitting corrosion in most reactors that are made of steel. Moreover, the high temperatures rapidly dilute the KCl solution used in the reference electrode, thus causing the potential of the reference electrode to drift.

The current trend has been the use of an external reference electrode at room temperature, where the electrode is held in a separate compartment and connected to the electrochemical reactor by means of a salt bridge. (W. Bosch, H. Zheng et al. 2003, Bogaerts 2016, Fleige, Wiberg et al. 2017) Thereby giving the researcher a choice from a wide range of traditional reference electrodes for high temperature electrochemistry use, in addition to limiting the exposure of the reactor to chlorides and eliminating the problem of hydrolysis. The major challenges faced by external reference electrodes are: (1) they have to be adapted such that their pressure is in equilibrium with that of the reactor and (2) The potential measurements require correction to account for thermal junction potentials, the calculation of which requires the knowledge of the heat transferred between the reactor and the reference electrode. Details of the calculation are explained in a recent publication by Bogaerts. (W. Bosch, H. Zheng et al. 2003, Bogaerts 2016)

Hydrogen electrodes namely reversible hydrogen electrodes (RHE) and dynamic hydrogen electrodes (DHE) have been predominantly used for fuel cell studies. (MacInnes and Adler 1919, Parthasarathy, Srinivasan et al. 1992) Another approach that has been adopted by for high temperature fuel cell studies, is the choice of the non-thermodynamic or pseudo-reference electrodes. This opens a window of opportunity for a wide variety of materials to be used as reference electrodes. The use of a pseudo-reference electrode can be useful, when one is only interested in performing kinetic studies and where one is certain of the redox potential of the targeted electrochemical reaction. (Han, Park et al. 2007), (Sampedro, Rosas et al. 1999, Kasem and Jones 2008) Normal calomel electrode has also been used for high pressure studies. Recently, non-thermodynamic reference electrodes also known as pseudo-reference electrodes (or) quasi-reference electrodes, such as tungsten (Tse and Gewirth 2015), Ag (Wiberg, Fleige et al. 2014, Fleige,
Wiberg et al. (2015), and Pt (Kasem and Jones 2008) wire, have also been used for ETP studies. The pseudo-reference electrode, however, requires calibration versus a standard electrode before use, which is normally done at operating pressures and temperatures with a redox-couple or a traditional reference electrode. A procedure to calibrate the reference potential with temperature was developed for Ag electrode versus dynamic reversible hydrogen electrode, which we have adopted for our study. (Wiberg, Fleige et al. 2014) Solid state reference electrodes have emerged as potential alternatives to the traditional counterparts, owing to their convenience in miniature reactors where employing a traditional reference electrode is difficult. (Han, Park et al. 2007) Mesoporous Pt (mPt) has been proposed as a reference electrode. (Attard, Bartlett et al. 1997) The typical oxidation states for Pt are Pt(II) and Pt(IV) as illustrated in Eqn. 1 below: (Whitfield 1974, Bard, Parsons et al. 1985)

\[ \text{Pt(s)} + \text{H}_2\text{O} \rightleftharpoons \text{PtO(s)} + 2\text{H}^+ + 2\text{e}^- \quad E^{\circ'} = 0.98 \text{ V} \]  

(11)

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Pressure</th>
<th>Temp</th>
<th>RE</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1922</td>
<td>Hainsworth, MacInnes</td>
<td>1-406 atm</td>
<td>25 °C</td>
<td>SCE</td>
<td>(Hainsworth and MacInnes 1922)</td>
</tr>
<tr>
<td>1924</td>
<td>Hainsworth, Rowley, MacInnes</td>
<td>1-1000 atm</td>
<td>25 °C</td>
<td>SCE</td>
<td>(Hainsworth, Rowley et al. 1924)</td>
</tr>
<tr>
<td>1953</td>
<td>Buchanan, Hamann</td>
<td>1-3000 atm</td>
<td>RT</td>
<td></td>
<td>(Buchanan and Hamann 1953)</td>
</tr>
<tr>
<td>1957</td>
<td>Ewald, Lim</td>
<td>1-3000 atm</td>
<td>RT</td>
<td>SCE</td>
<td>(Ewald and Lim 1957)</td>
</tr>
<tr>
<td>1963</td>
<td>Hamann</td>
<td>0-2000 atm</td>
<td>25 °C</td>
<td>Ag/AgCl</td>
<td>(Hamann 1963)</td>
</tr>
<tr>
<td>1977</td>
<td>Conway, Currie</td>
<td>0-2.2 kbar</td>
<td>RT</td>
<td>RHE on Pd</td>
<td>(Conway and Currie 1978)</td>
</tr>
<tr>
<td>1977</td>
<td>Conway, Kozlowska, Sharp</td>
<td>1 - 94 °C</td>
<td>Platinized Pt</td>
<td>(Conway, Angerstein-Kozlowska et al. 1978)</td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>Nagy, Yonco</td>
<td>100 atm</td>
<td>300 °C</td>
<td>Ag/AgCl</td>
<td>(Nagy and M. Yonco 1987)</td>
</tr>
<tr>
<td>1991</td>
<td>Krasinski et al</td>
<td>0.001 - 10kbar</td>
<td>RT</td>
<td>Ag/AgCl</td>
<td>(Krasiński, Tkacz et al. 1991)</td>
</tr>
<tr>
<td>1992</td>
<td>Cruanes, Drickamer, Faulkner</td>
<td>0-10 kbar</td>
<td>21 °C</td>
<td>Ag/AgCl</td>
<td>(Cruanes, Drickamer et al. 1992)</td>
</tr>
<tr>
<td>1995</td>
<td>Cruanes, Drickamer, Faulkner</td>
<td>0-6 kbar</td>
<td>RT</td>
<td>Ag/AgCl</td>
<td>(Cruanes, Drickamer et al. 1995)</td>
</tr>
<tr>
<td>1996</td>
<td>Gorecki, Golas</td>
<td>10 kbar</td>
<td>RT</td>
<td>Ag/AgCl</td>
<td>(Górecki and Golaś 1996)</td>
</tr>
</tbody>
</table>

Table 4 - List of reference electrodes used at high pressure electrochemical studies.
Therefore, in standard conditions Pt-oxide undergoes reduction to metallic Pt at potentials below 0.98V, which is well above the standard reduction potential for most metals. Additionally, from E-pH diagrams of Pt, it is observed that Pt exists in its metallic state at pH < 4 and Pt-oxides are stable only at pH > 4. Therefore, Pt can be used as a quasi-reference electrode in halide-free environments for studying electrodeposition of metals less noble than Pt. Park et al., prepared a pH-responsive mPt by oxidizing the ordered Pt deposits in a phosphate buffer reference solution. (Park, Boo et al. 2005) The authors used an electrodeposition procedure developed by Bartlett et al., to obtain the nanoporous Pt deposits. (Attard, Bartlett et al. 1997, Elliott, Attard et al. 1999) The uniform distribution of mesopores, of diameter below 10nm, allow for stable potential measurements. Therefore, it is of interest to investigate the behavior of the mesoporous Pt electrode as a quasi-reference electrode at high temperatures and high pressures.

2.8 THEORY OF CU ELECTRODEPOSITION


Based on CV studies with a hanging mercury drop in nitrate and perchlorate medium, the Cu deposition was set to follow the (C)ECE mechanism, with parallel deaquation-hydrolysis of Cu(II) and Cu(I) reactions constituting the chemical steps preceding each electrochemical step. The study also revealed that the deaquation-hydrolysis of Cu(I) species is the rate determining step in the pH range 0 to 5.6 in both nitrate and perchlorate medium.(Anderson and Shain 1976) However, the widely accepted mechanism involves two single-electron transfer steps with the Cu²⁺ and Cu⁺ ion in aqueous state, and surface diffusion as the major steps involved in copper electrodeposition.(Bockris and Kita 1962, Brown and Thirsk 1965, Reid and David 1987, Bimaghra and Crousier 1989, Jardy, Legal Lasalle-Molin et al. 1992, Wong, Coller et al. 1993, Kelly and West 1998) The major reactions that occur during the electrodeposition of copper at standard conditions (25 °C and 1 atm), from a sulfate solution is expressed in Eqns. 1-4.
Charge transfer $\text{Cu}^{2+}/\text{Cu}^+$

$\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+ \quad E^{0'} = 0.153 \text{ V} \quad (1)$

Charge transfer $\text{Cu}^+ / \text{Cu}$

$\text{Cu}^+ + e^- \rightleftharpoons \text{Cu} \quad E^{0'} = 0.521 \text{ V} \quad (2)$

Overall reaction $\text{Cu}^{2+} / \text{Cu}$

$\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu} \quad E^{0'} = 0.337 \text{ V} \quad (3)$

Comproportionation / Disproportionation

$\text{Cu}^{2+}_{aq} + \text{Cu} \rightleftharpoons 2 \text{Cu}^{+}_{aq} \quad K_{eq} = 6 \times 10^{-7} \text{ M} \quad (4)$

The rate determining step depends on the surface preparation, current density, and cupric ion concentrations. (Reid and David 1987) The formation of the cuprous ions is the rate determining step at higher current densities, whereas at lower current densities (an overpotential of less than 10mV) the surface diffusion of $\text{Cu}^+$ ions and lattice incorporation dictate the rate of copper electrodeposition. Eqn 4, represents the comproportionation reaction where $\text{Cu}^+$ ions are formed from the interaction between Cu and $\text{Cu}^{2+}$ or the disproportionation reaction which refers to the dissociation of $\text{Cu}^+$ ions to Cu and $\text{Cu}^{2+}$ ions. Despite the consensus in the above-mentioned reactions, some discrepancy still lies in the nature of the species involved in the reaction i.e., if they are adsorbed on the surface or in the aqueous solution phase. For instance, one such study reports that the $\text{Cu}^+$ ions are reported to revert back to $\text{Cu}^{2+}$ due to backstripping, whose rate increase with temperature, by reacting irreversibly with dissolved oxygen that arises from electrochemical reactions at the anode (Eqn. 5). Although, it should be pointed out that the evidence of the “backstripping” reaction has not been presented or disputed in any other study. (Shirvanian and Calo 2005)

Impedance studies on sulfuric acid - cupric sulfate system established that for both quiescent and agitated systems, the deposition is controlled by the charge transfer step $\text{Cu}^{2+}/\text{Cu}^+$ at the high frequency range. However, at the low frequency region, the quiescent solutions exhibited a Warburg feature, implying the diffusion of $\text{Cu}^{2+}$ ions to the surface took the role of the rate limiting step. On the other hand, the Nyquist plots for agitated systems features a smaller second semi-circle which has been attributed to the $\text{Cu}^+ / \text{Cu}$ reduction step coupled with surface diffusion. (Reid and David 1987)

Markovic et al., attributes the faster kinetics obtained for copper electrodeposition in bisulfate and chloride as opposed to perchlorate environments, based on results from RRDE studies, to the anions weak hydration. Voltammetric studies on rotating disk electrode studies, confirmed that copper electrodeposition is limited by $\text{Cu}^{2+}/\text{Cu}^+$ charge transfer step in a wide range of overpotentials and that at low cathodic overpotentials copper electrodeposition is independent of potential and limited by the diffusion of cuprous ions ($\text{Cu}^+$). By using Levich equation described below in Eqn. 6, the authors estimated the value of the equilibrium constant for the disproportionation reaction to be $K=3.4 \times 10^{-7} \text{ M.}$ (Schmidt and Gaida)

$$i_L = 0.620 n F D^2 \frac{1}{2} \omega^2 \frac{1}{6} v^{-1} C$$

where, $i_L$ is the limiting current density [A m$^{-2}$], $n$ is the number of electrons in the reaction, $D$ is the diffusion coefficient of the reacting species [m$^2$ s$^{-1}$], $\omega$ is the rotation rate [rad s$^{-1}$], $v$ is the kinematic viscosity [m$^2$ s$^{-1}$], $C$ is the bulk concentration of reacting species [mol m$^{-3}$]. Studies on rotating-ring disk electrode show that the deposition overpotential and plating rate are dependent upon the cuprous ion surface concentration. The presence of cuprous ions at the surface has shown to increase the copper deposition rate. (Vereecken, Binstead et al. 2005)

Electrochemical studies at elevated temperatures and pressures are not new and finds application in the fields of corrosion in supercritical fluids (Ubah and Asselin 2009) and in high-pressure oil pipelines, high-pressure electrolysis. (Onda, Kyakuno et al. 2004, Laoun 2007, Todd, Schwager et al. 2014) fuel cells, (Mcbreen, Ogrady et al. 1984, Parthasarathy, Srinivasan et al. 1992) batteries, (Makio 1931) geothermal chemistries, (Gallup 1993, Lazaro and Jeffrey 2006) and
supercritical fluids (Crooks, Fan et al. 1984, Hodes, Griffith et al. 2004). However, it has been documented that experimentation at these conditions have proven to be cumbersome and challenging. The choice of materials and achieving leak-tight seals at high pressures have been some of the main challenges which have hindered the proliferation of research in this area. (Giovanelli, Lawrence et al. 2004) Electrochemical studies at high pressures date back to 1904, where professor Arthur Noyes and his co-workers used high pressures as means to extend conductivities and ionization measurements for salts and acids to high temperatures. (Noyes and Coolidge 1903, Noyes 1904, Noyes 1907, Noyes, Melcher et al. 1908)

Approaches to pressurize a cell depends upon the choice of (A) a batch setup (Lewis and Randall 1914, Hainsworth and MacInnes 1922, Hainsworth, Rowley et al. 1924, Buchanan and Hamann 1953, Ewald and Lim 1957, Hamann 1963) where in the electrolyte in the reactor is pressurized by reducing the volume of the reactor with a piston or increasing the volume of gas by using a compressor or a high-pressure gas cylinder, (B) a continuous setup (Ubah and Asselin 2009) where the electrolyte can be supplied to the reactor at a high pressure by means of a pump working in tandem with a pressure regulator. Giovanelli et al., gives an extensive review of the various high-pressure setups used for electrochemical measurements prior to 2004, although they pertain to stationary electrodes alone. (Giovanelli, Lawrence et al. 2004)

Until now, no study has been reported on the effect of temperatures beyond 373 K on the electrodeposition of metals from aqueous medium.
3 Lab experiments

3.1 Experimental Setup

3.1.1 STATIONARY ELECTRODE – ETEP REACTOR

High pressure electrochemical experiments were carried out in the reactor as shown in Figure 3-1. Electrodeposition studies were performed at pressures up to 423 K and 50 bar on a stationary electrode. The reactor is constructed from SS316L, and equipped with a diaphragm type pressure gauge, K-type thermocouple, and a burst seal set at 100 bar. The reactor was then placed in a temperature-controlled silicone oil bath, (M1028/50, from Carl Roth GmbH), which was heated using a hot plate equipped with a magnetic stirrer.

![Figure 3-1. (A) 3-D model with reactant chamber and (B) cross-sectional view illustrating the internals of the High pressure Electrochemical Reactor setup, used for reference electrode calibration](image)

3.1.2 REFERENCE ELECTRODE PREPARATION

A mesoporous Pt (mPt) electrodeposited onto a Pt wire of diameter 1 mm sealed in a glass casing was used as a pseudo-reference electrode. Electrodeposition was carried on a platinum disk substrate for electrochemical studies. The substrate was attached to a glassy carbon electrode by means of a conducting carbon tape. Platinum disk electrodes were prepared by encapsulating a platinum wire of diameter 1 mm in soft glass. The Pt disk was then polished with 800 and 1200 grade sand paper, followed by buffing with alumina particles of size 6, 3, and 0.7 microns in the mentioned order to obtain a mirror finish observed using an AxioCam ERc 5s optical microscope manufactured by Carl Zeiss Microscopy GmbH. The platinum surface was subsequently treated with aqua regia and 10% nitric acid to remove any contaminants that may have carried from the polishing steps. This was followed by alkaline cleaning with VR6334-16 (40 g l⁻¹) at 65 °C in an ultrasonic bath for 15 min. The wires were then degreased with acetone and rinsed with DI water. Any surface oxides that could have been formed from the previous steps were removed electrochemically by cycling in the in 1 M sulfuric acid at hydrogen evolution potentials between -0.22 V and 0.2 V versus silver-silver chloride.
with saturated KCl reference electrode (Ag/AgCl), until reproducible cycles were obtained at 100 mV s⁻¹.

Platinum electrodeposition was carried out in a bath made with octaethylene glycol mono hexadecyl ether, dihydrogen hexachloroplatinate, and deionized water, taken in the ratio 0.3 : 0.2 : 0.5 (by weight), respectively. The plating solution was heated to 80 °C to obtain a homogeneous solution. The electrodeposition was carried out at -0.06 V vs Ag/AgCl at temperatures between 25 °C and 65 °C electrode for a certain charge. Following the deposition, the electrode was subject to cleaning by immersion for a period of 24 h in 10 ml of deionized water, where the water was replaced every 3 hours.

### 3.1.3 ETP-RDE REACTOR SETUP DESCRIPTION

The process flow piping and instrumentation diagram for the setup, and a detailed schematic of the reactor is shown in Figure 1 and Figure 2, respectively. The setup consists of a stainless steel 316L vessel V1 sealed with SS316L lid, pressurized with the help of high-pressure and high purity (99.99%) nitrogen and oxygen gas cylinders rated at 200 bar from Air Liquide. The reactor is designed for a maximum operating temperature (Ts) for the vessel of 300 °C (an intended maximum operating temperature of 250 °C with a 20% surge) and maximum operating pressure (Ps) is 200 bar, based on the maximum delivery pressure from the compressed gas tank.

![Diagram](image)

**Figure 3-2. Process flow, Piping and Instrumentation diagram for the ETP-RDE reactor setup.** PCV - back-pressure regulator, PSV Pressure Safety Valve, MV Manual Valve, PI - Pressure Indicator, TI - Temperature Indicator, TIT – Temperature Indicator Transmitter.

The pressure inside the reactor is controlled using a back-pressure regulator (Tescom 44-1100 from Emerson) at the gas outlet, labelled PCV-V1 in Figure 1. The pressure in the vessel is monitored with two manometers, for redundancy, an analog pressure gauge labelled PI placed at the gas inlet line and a digital manometer labelled PIT to send data to the computer at the outlet line. The vessel has provisions to be heated by three 650 W electrical heating tapes connected parallel and wrapped around the vessel, to provide uniform heating along the height of the vessel and a conducting copper plate at the bottom. The vessel is insulated to avoid exposure of hot surfaces. The vessel has provision for a type-K thermocouple labelled TI to measure the temperature inside the vessel, and a PT100 temperature sensor labelled TIT located at the vessel wall. The TIT sends temperature feedback to a temperature controller (EPC-3016 from Eurotherm) that controls the voltage supplied to the 650-Watt electrical heating tapes (MBH-4515650T) manufactured by Omegalux that are connected in parallel configuration.
Figures 3-3A and 3-3B illustrate a schematic of the high pressure system and the control unit. As shown in Figure 3-4A, the lid screws onto the vessel with buttress threads and an air-tight seal is achieved by a set of Kalrez® (Dupont), a perfluroelastomer, O-rings stable at temperatures up to 327 °C. The pipeline for the vessel, the inlet port and outlet ports are made of stainless steel 316L from Swagelok and they are rated at 300 bar. The vessel has four banana-plug type electrical connections that are press-fitted with high-pressure feed through contacts with PEEK seals (from Spectite) that provides connections to two working electrodes, a reference electrode, and a counter electrode from a potentiostat. As shown in 3-4B, a solid stainless-steel shaft with mount for the rotating-ring disk electrode is housed inside a PEEK housing and along the centerline of the vessel. Electrical connections from the electrodes to the banana plugs are achieved by 4-silver/graphite slip-ring contacts. Zirconia bearings connect the shaft to a pair of Sm-Co magnets inside the vessel that is coupled with another pair of Sm-Co magnets placed outside the vessel. The outer magnets are housed in an aluminum casing that is directly mounted to the bottom of a standard rotating disk motor (EC-max40 from Maxon) by means of a metal-silicone-metal coupling. The rotation rates are calibrated with a non-contact tachometer to measure the rotations per minute (rpm). All instruments (pressure gauges, thermocouples, control and manual valves) are rated at 300 bar.

Working electrode design (depicted in Figure 3-4B): A traditional rotating disk electrode consists of an electrode constructed from a rod of the interested material of a defined area with the axis of rotation passing through its center. This electrode is sealed with a non-conducting, non-porous resin such that the disk exposed to the electrolyte is flush with the sealant such that the diffusion layer is in a laminar region at rotation speeds of up to 4000 rpm. The masking material of choice is usually a polymer of the type PTFE, or PEEK, or PAI.(Oppkar and Beran 1976) However, despite being chemical stable, they are not recommended to be used at high temperatures due to their exceedingly high coefficient of thermal expansion which can disrupt of the electrode-masking geometry and possibly cause turbulence in the diffusion layer. Care should be taken, while designing an RDE, that the defined electrode geometry and area maintained during operation at elevated temperatures. Additionally, the sealing material should be resilient enough (i.e., not brittle) to handle any radial expansion of the electrode / current collector at high temperatures. Literatures shows that boron nitride, Macor, and borosilicate has been used as sealing material for Mo, Pt, and glassy carbon electrodes respectively while using titanium or nichrome as the current collector.(Phillips, Gale et al. 1976, Roe and Aparicio-Razo 1984, Stojanovic, Kubacki et al. 1995) After extensive studies, the RDE was designed with a Macor shell such that it could be used with any electrode material clamped with an appropriately sized titanium core. Titanium also acted as our current collector. The length of electrode material is chosen to be equal to the product of the Macor height and the ratio their CTE. The housing height of the titanium is adjusted to account for the additional height of the electrode.

*Figure 3-3 Rotating Electrode – ETEP reactor system with control unit, with safety instruments used for estimating kinetic and transport properties of electrochemical reactions at temperatures up to 300 °C and 238 bar.*
Figure 3-4. (A) Cross-sectional view of ETPER manufactured (B) High temperature and pressure rotating disk electrode designed to operate at 200 bar and 300 °C.

**RISK ASSESSMENT AND SAFETY TEST**

A risk assessment was performed on our setup with the process safety team at KU Leuven. Details of the risk assessment involved the review of the standard operating (supporting information), and the performance of a Hazardous Operability (HAZOP) and failure modes study (supporting information). Article 4 of the PED, explicitly obviates the requirement for our pressure vessel to be CE stamped. However, requires sound engineering practices to be incorporated. Based on the literature and our experimental plans, the intended operating pressure and temperature is 100 bar and 250 °C. To ensure sound engineering practice, the design pressure \( P_D \) i.e., the maximum pressure for a vessel that accounts for material of construction, dimensions, pressure surges, and stresses imposed during normal operation and maximum allowable working pressure (MAWP) i.e., the maximum pressure for a certain operating temperature, were calculated.
Table 5. Calculation of design pressure ($P_d$), maximum allowable working pressure (MAWP), and hydrotest pressure ($P_t$) of the ETP-RDE reactor. The orange cells indicate input values, whereas the gray cells are calculated values.

For a particular temperature, the MAWP is initially higher than the design pressure and it varies over time as the vessel ages, due to corrosion and vessel fatigue. No explicit formula for the calculation of the design pressure and MAWP is suggested in the EU-PED, they were calculated based on formula recommendations listed per American Society of Mechanical Engineers (ASME) for pressure vessels. The design pressure is estimated from the vessel wall thickness, the internal and external stress experienced by the vessel during normal operation, decreased by a safety factor of 2 to account for probable pressure surges. Pressure rating calculations to estimate the maximum allowable working pressure (MAWP) of 470 bar at 250 °C was evaluated by TUV Rhineland. The calculations show that design pressure is 238 bar at 300 °C, whereas the MAWP is 272 bar at 300 °C, and a hydrotesting pressure of 298 bar. Details of the calculations and the basis for the calculations are listed in Table 5.

Hydrotesting, is performed to ensure that a pressure vessel can safely operate at its calculated design pressure. It is carried out by pumping water in to the equipment until a predetermined pressure is reached and maintained at that pressure for an hour. Details to obtain the pressure for hydrotesting, are outlined by the European Union - Pressure Equipment Directive (PED 2014/68/EU). This begins with the classification of the equipment on the EU-PED Article 4.1(a)(i), our ETP-RDE is classified based on Table 1 in Annex II of the PED, since our reactor is designed to handle oxygen (Group I fluid) and the product of Ps and the volume of the vessel ($V = 270$ ml) at 54...
bar-l which is greater than the specified 25 bar-l. Additionally, based on Article 4.2, our reactor is classified as a heated pressure equipment. Based on the above classification, EU-PED directs that our reactor shall meet all essential safety requirements listed in the Annex 1 of the directive, which includes the estimation of the hydrotesting pressure. Per the directive, the equipment shall be hydrotested at a pressure that is greater amongst 1.25 x design pressure (P_D) and 1.45 x maximum operating pressure (P_s). The definitions for the terms P_s and maximum operating temperature (T_s) amongst others are explained in Article 2 of the EU-PED mentioned above.

Hydrotesting was performed with the help of a cold isostatic press (CIP), manufactured by Engineered Pressure Systems International N.V, designed to reach water pressures up to 3000 bar with the help of compressed air. Hydrotesting was achieved by presetting the water pressure to 300 bar and redirecting the water from the press in to the ETP-RDE reactor. The pressure was recorded at the start and end of the experiment after 1 hour. No deformation or leaks were observed during this test, thereby assuring us that the vessel can safely be rated to operate at the design conditions of 239 bar and 300 °C.

**Installed safety devices:** Our first line of safety will rely on good engineering practices which includes a backpressure regulator located downstream of the reactor and set at the process pressure to control the pressure in the reactor equal to or below the set pressure. Secondly, we have an inlet solenoid safety valve (ERA, France), which is normally closed. Upon the start of the experiment a current signal is sent to the safety valve to open it and stay opened until the reactor reaches a specified maximum pressure, when the power supply to the safety valve is cut-off, this results in its closing thereby isolating the vessel from the gas cylinder. The maximum pressure for the solenoid valve (P_max) will be set at the beginning of each experiment at 10% above the process pressure for that experiment. Upon loss of pressure control in the reactor, due to an unintended runaway reaction, a pressure relief valve and a burst seal is used to protect the operator and the reactor. The pressure relief valve (from Fitok) that is set to operate between the pressures 103 bar and 172 bar. A burst seal is set to be triggered at 240 bar, in case of pressure relief valve failure, thereby preventing further increase in pressure in the reactor. Finally, as a part of the safety system – a mechanical emergency button is installed, which shuts off the power supply to the heater and the inlet solenoid valve.

### 3.2. Materials and Methods

**Reagents:** Deposition solutions were made from analytical grade CuSO_4·5H_2O obtained from Sigma Aldrich. Concentrated Sulfuric acid and nitric acid were obtained from Acros Organics. The concentration for all solutions reported in the paper were prepared at 293 K and 1 atm. Nitrogen of purity 99.99 % from Air Liquide was used as the pressurizing gas. Reticulated vitreous carbon (RVC) with a bulk density of 0.05 g cm^{-3}, porosity of 96.5%, 24 pores cm^{-1} and thickness 6.35, as rolled Pt foil of thickness 0.025 mm with a geometric area 1.76 cm^2, Cu sheets of 1 mm, and annealed Pt wire of diameter 0.125mm and purity 99.95%, were obtained from Goodfellow.
**Working Electrode Preparation:** For cyclic voltammetry GC was used as the working electrode and the Pt foil was used as the counter electrode. For the recovery studies RVC of thickness 0.6 cm and diameter 2.8 cm was used as the working electrode, while a RVC electrode with a similar diameter and a thickness of 1 cm was used as the counter electrode. The GC and RVC electrodes were pretreated by exposing them to 3 M HNO₃ solution for 60 seconds, followed by washing with water and ethanol, followed by air drying at 383 K. The RVC electrode was then weighed prior to each recovery study.

![Image]( figure3-5.jpg)

*Figure 3-5. RVC electrodes placed in a glass beaker for depicting, how they will be placed inside the stainless steel reactor. Electrodeposition on RVC electrode, enclosed in the PEEK holder with a titanium foil lining the interior portion of the holder, which allows for uniform distribution of current around the RVC electrode in addition to serving as a current collector.*

**Electrochemical studies** were carried out in using an Autolab PGSTAT302N potentiostat. Prior to starting the electrochemical studies at ETEP, proper working of the reference electrode was verified by recording a stable and constant OCP versus a commercial Ag/AgCl and the signature CV of Pt in 0.1 M H₂SO₄ at room temperature and pressure. The reactor was charged with 50 ml of the plating electrolyte solution, sealed, and pressurized using nitrogen gas. All experiments were performed in 10 mM CuSO₄ and 100 mM H₂SO₄ electrolyte solution unless otherwise mentioned. The ratio of sulfuric acid concentration to copper sulfate was chosen based on a statistical study for optimal copper deposition, which maximum efficiency was obtained for electrodeposition. The solution resistance between the working and reference electrode was estimated by impedance spectroscopy at high frequencies. The limits for parameters evaluated are displayed in Table 6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>High</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>423</td>
<td>298</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>Electrodeposition Potential (mV)</td>
<td>-700</td>
<td>-575</td>
</tr>
<tr>
<td>Initial Cu concentration (mM)</td>
<td>2.5</td>
<td>10</td>
</tr>
<tr>
<td>Time (min)</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

*Table 6. limits of the various parameters used in the OFAT study for copper recovery.*

The copper concentrations in the solution were measured before and after each electrodeposition study. The Cu concentrations were obtained from absorbance spectrum measurements from a Varian 2000, an inductively coupled plasma – optical emission spectroscopy (ICP-OES), at 240 nm. The ICP-OES equipment was calibrated in the range 1 ppm to 100 ppm, prepared by diluting a 1000...
ppm calibration standard in 3 % HNO₃ solution. Each measurement was done in triplicates, to avoid carry-over from previous solutions.

**Surface Morphology and Crystal Structure Characterization:** Surface morphology of the deposits were studied using a Philips XL30 FEG scanning electron microscope (SEM) operating at 10kV. High resolution electron micrographs were obtained using a JEOL-ARM200F transmission electron microscope (TEM) operating at 200kV. The crystal structure of the deposits was measured using Seifert 3000 T/T X-ray diffractometer using Cu-Kα radiation (λ = 1.54 Å) in the 2θ range between 25° and 80°, with a resolution of 0.02° and a rate of 1s per step.
4 Results and discussion

4.1 Reference electrode characterization and calibration

Mesoporous platinum was successfully electrodeposited onto Pt disk substrates and confirmed from SEM studies. Figures 4-1 A through 4-1C, shows the electron microscopy images obtained for the mesoporous Pt deposition performed 25 °C, respectively. From the SEM images, it can be observed that the deposition exhibits a porous structure. It can be observed from the TEM images that the diameter of the pores are in the 2 nm to 5 nm range, confirming that the deposits indeed form a mesoporous structure.

![Electron microscopy images of mesoporous platinum deposits synthesized by electrodeposition at 25 °C for a charge of 52 mC cm⁻². (A) Secondary emission image from SEM shows the porous deposits. (B) TEM image indicating an end-on view of the (C) TEM image indicating a side view of the pores, highlighted by the dashed circles. The pores exhibit a diameter in the 2 nm – 5 nm range, confirming a mesoporous structure.](image)

**Figure 4-1.** Electron microscopy images of mesoporous platinum deposits synthesized by electrodeposition at 25 °C for a charge of 52 mC cm⁻². (A) Secondary emission image from SEM shows the porous deposits. (B) TEM image indicating an end-on view of the (C) TEM image indicating a side view of the pores, highlighted by the dashed circles. The pores exhibit a diameter in the 2 nm – 5 nm range, confirming a mesoporous structure.

**Stability, Precision, Sensitivity, S/N Ratio, and Dynamic Response Measurement:** Open circuit potential (E_oc) measurements for the mPt electrode versus Ag/AgCl at room temperature and pressure were carried out with standard pH calibration solutions. The solution was continuously stirred at 250 rpm before measuring the potential, to avoid inconsistencies due to localized effects. The E_oc was said to be in steady state upon reaching a potential variation (dEoc/dt) was less than 3 \( \mu \text{V s}^{-1} \). The Eoc recorded for a period of 30 min after reaching the steady state. The steady state Eoc was recorded for mesoporous Pt electrode in each standard pH buffer solutions in the range between 4 and 12. **Stability** of the electrode was confirmed by recording steady state potentials ±1
µV for a period of 2 hours in the pH range between 4 and 12. Figure 2-3 illustrates the change in open circuit potential as a function of pH. It can be observed that a slope of 58.6 mV pH and a y-intercept of 775.6 mV was recorded for the synthesized reference electrode. The precision of the voltage readings at steady state, which is a measure of standard deviation is estimated from the standard deviation, was found to be ±1 µV.

The Sensitivity, or the least count is a measure of the smallest measurable change in potential, and the dynamic response of the electrode was estimated by acid-base potentiometric titration. This involves the measurement of changes in EOC for the mPt electrode vs Hg/HgSO4 in a continuously stirred basic solution (1M NH4OH), due to a change in pH realized from the addition of small volumes of an acidic solution (1 M CH3COOH). Sensitivity (i.e. changes as small as 0.1 mV was measured. The response rate, the time taken to reach new steady state potential, was estimated to vary between 1 and 3 s for any pH change.

![Figure 4-2](image)

*Figure 4-2. (A) Steady state Eoc recorded by mPt electrode, in various standard pH buffer solutions obtained from Metrohm, Hanna Instruments, and Centripur. (B) Dynamic potential response of mPt electrode in a solution of 1M NH4OH due to pH change caused by addition of 1M CH3COOH.*

The chemical stability and robustness of mPt electrode was evaluated by evaluating the electrochemical active surface area from hydrogen adsorption in acidic media before and after exposure to 0.1 M acidic media at 423K and 50 bar, using the setup described above. The hydrogen adsorption studies was performed at room temperature and pressure (298 K and 1 atm). The electrochemically active surface area of the electrodes was determined by estimating the hydrogen adsorption charge from cyclic voltammetry experiments. The electrode was stored used as a RE at 423 K and 50 bar for approximately another 24 hours, after which another hydrogen adsorption study at room temperature was done. The results of the above study, the cyclic voltammogram of the Pt electrode in 1 M H2SO4 once prepared, after exposure to 423K and 50 bar, and after use as RE at temperatures up to 423 K and pressure up to 50 bar, are shown in Figure 2-4. It can be observed that, no significant change in the hydrogen adsorption and electrochemical active surface area have been identified, before and after exposure to high temperature and pressure, as well as after its use as a RE at elevated temperatures and pressures. This can be attributed to the possibility
that even at high temperatures and pressures, in acidic medium, the formation of Pt-oxides continue to be shunned thereby preserving the metallic form of Pt.

Figure 4-3. Cyclic voltammogram of mPt in 1 M sulfuric acid at 100 mVs\(^{-1}\) before and after 24 hours of exposure to 0.1 M sulfuric acid at 423K and 50 bar

Figure 4-4. (A) Typical cyclic voltammogram for the Fe(II)/Fe(III) redox couple. The CV was performed on a glassy carbon working electrode in a solution of 1 M PBS solution containing 10 mM K\(\text{Fe(CN)}_6\) with mPt quasi-reference electrode, and a Pt foil counter electrode at 100 mV s\(^{-1}\). (B) CV’s Fe(II)/Fe(III) redox couple performed at temperatures ranging from 298 K to 423 K, and a pressure of 50 bar. (C) The standard potential of Fe(II)/Fe(III) for the redox couple plotted as a function of temperature.
Calibration of $E_{\text{mPt}}$ as a function of temperature and pressure: The mPt electrode was calibrated by studying the variation in the redox potential for the Fe(II)/Fe(III) reaction with temperature at high pressure. From Figure 2.5C, it can be observed that the equilibrium potential of Fe(II)/Fe(III) redox couple measured with respect to Pt quasi-reference electrode varies with temperature based on the expression displayed in the figure. In addition to the variation of the Fe(II)/Fe(III) redox potential, the expression in Fig. 2.5C, includes the variation of the potential of the mPt quasi-reference electrode with temperature. It has been previously shown that the equilibrium of Fe(II)/Fe(III) redox couple varies as a function of temperature and the relationship is given by the below expression:

$$E_{\text{Fe(II)/Fe(III)}} = 0.43028 - 2.5157 \times 10^{-3}(T - 298) - 3.7979 \times 10^{-6}(T - 298)^2$$  \hfill (12)

where, $E_{\text{Fe(II)/Fe(III)}}$ is the redox potential for Fe(II)/Fe(III) expressed in V vs SHE, and $T$ is the temperature in K. Upon eliminating the contribution of the Fe(II)/Fe(III) redox couple from expression in Fig. 2.5 C, the potential of the mPt quasi-reference electrode as a function of temperature is found to be

$$E_{\text{mPt(Fe$^{2+}$/Fe$^{3+}$)}}(\text{vs SHE}) = 0.6108 - 2.5 \times 10^{-3}(T - 298)$$ \hfill (13)

where, $E_{\text{mPt}}$ is the equilibrium potential of the mPt quasi-reference electrode expressed in V vs SHE, and $T$ is the temperature in K. The coefficient of second order term is in the order of $10^{-6}$, and ignoring the second order term did not significantly affect the results. The equilibrium potential of the mPt quasi-reversible electrode is found to vary linearly with temperature.

A dynamic RHE was simulated by producing hydrogen in-situ on a Pt wire electrode that was sealed in a glass tube. Hydrogen was produced for 1 minute followed by measuring the open circuit potential between the RHE and Pt-Pt oxide electrode was measured for a duration of a few seconds. The experiment was carried out at 50 bar at various temperatures between 298 K and 423 K. The temperature for each run was varied incrementally from lower temperature to a higher temperature. Upon reaching 423 K the measurements were repeated by varying the reactor from the higher temperature to a 298 K, by cooling the reactor. The potentials observed in the incremental temperature experiments matched with the potentials measured while the temperatures was gradually reduced back to 298 K, indicating that the electrode is stable after usage at high temperatures. The OCP data vs mPt electrode was recorded versus time, as shown in Figure 2-6A, the potential varied rapidly within a few seconds, which can be attributed to the loss of hydrogen from the glass tube. Therefore, the potential at zero time, was correlated with the maximum hydrogen present at the electrode surface, and was noted as the OCP of the RHE versus mPt electrode. This OCP was subsequently plotted versus temperature as shown in Figure 2-6B. A linear regression, with 95% confidence limits, of the data showed that the standard equilibrium potential of mPt electrode as a function of temperature to be 3.1 mV K$^{-1}$. Upon correcting for the potential variation due to (1) change in equilibrium potential of RHE (0.84 mV K$^{-1}$) and (2) variation of pH (0.198 mV K$^{-1}$) as a function of temperature, the standard equilibrium potential of the mPt electrode vs a pH independent SHE is given in Equation 14.

$$E_{\text{mPt(H$^+$/H$_2$)}}(\text{vs SHE}) = 0.5007 - 2.5 \times 10^{-3}(T - 298)$$ \hfill (14)
The calibration with a dynamic hydrogen electrode also shows that the standard equilibrium potential of the mPt electrode varied linearly with the same slope, as was observed with the calibration obtained from Fe(II)/Fe(III) redox couple. Additionally, the slope of the standard equilibrium potential of the mPt electrode as a function of temperature obtained from the two methods were identical. However, the calibration with the hydrogen electrode was 100 mV lower than the calibration obtained using the Fe(II)/Fe(III) redox couple. This could be attributed to the fact that the rapid loss of hydrogen from the electrode surface, before the potentiostat was able to switch from chronoamperometric mode to measure mode in open circuit conditions.

**Figure 4-5.** (A) Open circuit potential of an in-situ dynamic RHE, in 0.1 M H$_2$SO$_4$, as a function of time, measured at several temperatures ranging between 298 K and 423 K. The potential at $t = 0$ s corresponds to the equilibrium potential of the RHE. (B) A plot of the equilibrium potential of the RHE as a function of temperature.
4.2 EFFECT OF TEMPERATURE AND PRESSURE ON Cu ELECTROCHEMISTRY

The effect of temperature and the activity of the redox species on the equilibrium potential of an electrochemical reaction is explained by the Nernst equation. At standard conditions (298 K and 1 atm) the equilibrium potential for the two-electron reduction of copper is given by Eqn. 9.

\[
E_{(\text{Cu}^{2+}/\text{Cu})} = E^0 + \frac{2.3RT}{2F} \log(a_{\text{Cu}^{2+}}) 
\]

where \(a_{\text{Cu}^{2+}}\), \(Y_{\text{Cu}^{2+}}\), and \(C_{\text{Cu}^{2+}}\) is the activity, activity coefficient, and concentration of Cu\(^{2+}\) ions in solution, respectively. For a solution of \(C_{\text{Cu}^{2+}} = 0.01\) M, the corresponding activity coefficient of the solution \(Y_{\text{Cu}^{2+}} = 0.158\), the reduction potential for Cu\(^{2+}\) to Cu estimated from Equation 9 is 0.266 V versus SHE (i.e., 0.067 V versus Ag/AgCl with saturated KCl). The effect of pressure on the reversible potential for any electrochemical reaction is given by the following expressions

\[
\Delta V^0 = \left( \frac{\partial (\Delta G^0)}{\partial P} \right)_T = -nF \left( \frac{\partial E^{0'}}{\partial P} \right)_T
\]

\[
E_2 - E_1 = \frac{RT}{2F} \ln \left( \frac{P_2}{P_1} \right)
\]

where, \(\Delta V^0\) is the standard volume of reaction [mol dm\(^{-3}\)] i.e., difference between the standard partial molar volumes of products and reactants, \(P\) is the pressure [Pa], \(\Delta G^0\) is the change in Gibbs free energy of the reaction [J mol\(^{-1}\)], \(dE^{0'}\) is the formal or equilibrium potential [V], and \(n\) is the number of electrons in the reaction, \(E_1\) and \(E_2\) are the equilibrium potentials expressed [V] at pressures \(P_1\) and \(P_2\), respectively.

Pourbaix (or potential-pH) diagrams represents the phases present in the aqueous electrochemical system at various potential and pH conditions. Beverskog and Puigdomenech (Beverskog and Puigdomenech 1997) extended these diagrams for copper at a pressure of 1 bar and temperatures up to 300 °C, which can help us in understanding the various phases one can expect at these higher temperatures. Figures 4-6A through 4-6D illustrates the simulated E-pH diagrams for Cu-H\(_2\)O system at different temperatures and pressures using HSC software version 5.0. Each solid line in the diagram represents the potential as a function of pH for an electrochemical reaction and it is estimated from the Nernst equation corresponding to that reaction. The dotted lines represent the potential for hydrogen evolution and oxygen evolution reaction. The region between the dotted lines in the diagram represents the region where water is stable. The E-pH diagram (Fig. 4-6A), estimated at 373 K and 1 bar, accurately reproduced the diagram from the literature, except for the Cu(OH)\(_2^-\) at pH above 11. This is attributed to the absence of the species in the HSC database for version 5.0. Additionally, this version software did not allow us to manually insert a new species to account for the missing Cu(OH)\(_2^-\).
Figure 4-6. Potential-pH diagrams for Cu-H₂O systems that were simulated using HSC software ver. 5 at (A) 373 K and 1 bar, (B) 293 K and 1 bar, (C) 293 K and 50 bar, and (D) 423 K and 50 bar. The concentration of copper is set at 1x10⁻⁶ M for Figure A and 0.01 M for Figures B to D.

A comparison of Figures 4-6B (293 K and 1 bar) and Figure 4-6C (293 K and 50 bar) sheds light on the effect of pressure on the aqueous copper chemistry. It can be observed that there is little to no difference in the E-pH diagrams at these two conditions, suggesting that the effect of pressure on the thermodynamic potentials of redox species in condensed phases are negligible. On the other hand, the effect of temperature on the redox potentials for Cu-H₂O system can be studied by comparing the Figures 4-6C (293 K and 50 bar) and 4-6D (423 K and 50 bar). The diagram at 250 °C shows the introduction of two new phases Cu⁺ at pH below 3 and CuO₂⁻ at pH above 12.5, in turn proving the stability of the newly formed phases at high temperatures. The increased stability of Cu⁺ ions at high temperature could be due to the rate of the comproportionation reaction, whereas the increased stability of CuO₂⁻ ions is attributed to the hydrolysis of copper that is predominant at temperatures between 373 K and 573 K. The study has shown that additional phases corresponding to Cu(OH)₇⁺, Cu(OH)₅⁺ and Cu(OH)₃NO⁺ ions are present at lower copper concentrations even at a temperature of 293 K as the copper concentration is lowered from 10⁻⁶ mol kg⁻¹ to 10⁻⁸ mol kg⁻¹. Additionally, as the concentration is lowered the stability of the above-mentioned phases are said to increase.

Cyclic voltammetry was used to understand the electrochemical behavior of copper sulfate - sulfuric acid system. The voltammograms were recorded by sweeping the electrode from open circuit potential in the negative direction, until hydrogen evolution was observed, indicated by an exponential rise in the negative current is observed. Then the potential sweep was reversed, to
proceed the positive direction. The voltammograms were repeated until reproducible voltammograms were obtained from subsequent cycles.

Figure 4-7 shows a typical cyclic voltammogram (CV) of glassy carbon electrode (1 mm diameter) in 0.1 M sulfuric acid in the presence and absence of 0.01 M CuSO₄ at 25 °C and 1 atm. The dashed line represents the baseline voltammogram of 0.1 M sulfuric acid in the absence of copper ions. As expected, it shows a clean background voltammogram without any peaks. However, in the presence of CuSO₄, the voltammogram exhibits two peaks: one reduction / cathodic peak at -0.8688 V and one oxidation / anodic peak -0.4684 V. The reason for the presence of only one reduction peak, as opposed to two peaks for the two single-electron reduction reaction of Cu²⁺ / Cu⁺ and Cu⁺ / Cu as expressed in Eqns. 1 and 2, is attributed to the fact that the equilibrium potentials for the two reactions are fairly close to one another that the currents from each reaction overlaps, resulting in a single cathodic and single anodic peak. Also, the Cu²⁺/Cu⁺ charge transfer reaction has been reported to be the rate controlling step, implying that the Cu⁺ ions are consumed as they are formed. This sequence of electrochemical reactions where the first step is a rate determining step and the second step is a fast reaction, as in the EE reaction which are typically characterized by one peak in the CV and a single slope in kinetic controlled region of the linear sweep voltammetry studies. The peak separation (ΔE_p/n) is estimated to be 200 mV per electron transferred, implying a quasi-reversible reaction.

**Pressure effects** on the electrochemical behavior of aqueous copper sulfate system was studied using CV experiments were carried out on glassy carbon substrate at pressures of 1 bar and 50 bar at 293 K. Figure 4-8 shows the comparison of cyclic voltammograms for a glassy carbon electrode at 1 bar and 50 bar in the electrolyte with the presence and absence of Cu²⁺ ions. From Figure 4, it is observed that both the anodic and cathodic peaks corresponding to copper oxidation and reduction, at both 1 bar and 50 bar are identical, except for a slight increase in the anodic and cathodic currents. Thereby implying that the effect of pressure on condensed phases i.e., liquids (and solids), is minimal. The results confirm the observations in literature, where it has been proven that the effect of pressure on condensed phases appear only at pressures over 1000 bar or in complex
solutions where the metal ion is strongly coordinated such that the effect of metal center charge on the medium is extremely low.

![Figure 4-8. Comparison of cyclic voltammograms (5th cycle) for aqueous copper system performed at pressures of 1 bar and 50 bar. Both CV’s were performed at 293 K on glassy carbon electrode at 100 mV s⁻¹ in a 10 mM CuSO₄ + 100 mM H₂SO₄ solution and a Pt foil counter electrode. Pressure was maintained with nitrogen.](image)

**Temperature effects** on the aqueous copper electrochemistry was studied by performing CV experiments on glassy carbon electrode at temperatures of 293 K and 423 K, at a pressure of 50 bar for both experiments. The results of the study are presented in Figure 4-9A abd Figure 4-9B, which indicate enhanced reduction currents at potentials corresponding to cupric and cuprous ion reduction as well as hydrogen evolution. At first, the voltammogram appears noisy with many peaks. Therefore, to better understand the processes at high temperature, the CV was repeated in a narrow potential window where water electrolysis is avoided and this voltammogram is presented in Figure 5B. To help the reader, the negative and positive going sweeps are differentiated in the figure by solid and dashed lines, respectively. Upon close inspection one can see that the reduction currents can be broadly demarcated to three main reduction peaks, marked by peak ‘a’ at -0.60 V, peak ‘b’ at -0.79 V, and peak ‘c’ which is more of a shoulder occurs at -1.02 V in Figure 5B. It is noted that peak ‘a’ occurs at a voltage that is 130 mV more negative than the peak potential for the system at 20 °C. The reason for the three peaks at higher temperatures, could be attributed to the enhanced rates for comproportionation reaction, which results in the formation of Cu⁺ ions at the electrode surface, resulting from the Cu²⁺ ions from the solution and Cu on the electrode surface. This theory is corroborated by the increase of Cu⁺ phase with the increase in temperature as reported in the E-pH diagrams earlier. This then, leads to an enrichment of the Cu⁺ ions on the vicinity of the electrode surface, thereby depleting or reducing the concentration of the Cu²⁺ ions near the surface, in turn reducing the Cu²⁺ reduction currents, the increase in the Cu⁺ concentration then results in a prominent Cu⁺ peak. Therefore, we can relate the second peak ‘b’ to the Cu⁺/Cu charge transfer reaction. Proceeding further in the negative direction Cu⁺ is consumed, leading to the drop in Cu⁺ concentration at the interface as the diffusion of Cu⁺ to the surface controls the currents. The third peak could be associated to a second wave of Cu²⁺ reduction as the interface is cleared of Cu⁺ ions. However, for this second wave to occur at 400 mV more negative than the first peak, suggest that the diffusion of Cu²⁺ ions have to be increased in such a manner to bring back kinetic control 400
mV after it reached the first peak and 550 mV after the system at 20 degrees went into diffusion. Calculation of concentration independent diffusion coefficients is illustrated in Section 5.4.

**Figure 4-9.** Comparison of cyclic voltammograms (5th cycle) for aqueous copper system performed at temperatures of 293 K and 423 K. Both CV’s were performed at a pressure of 50 bar on glassy carbon electrode at 100 mV s\(^{-1}\) in a 10 mM CuSO\(_4\) + 100 mM H\(_2\)SO\(_4\) solution and a Pt foil counter electrode. (B) Voltammogram between -0.2 V to -1.2 V, negative and positive sweep are represented by solid and dashed lines, respectively.

**Effect of temperature and pressure on the transport parameters:** The diffusion coefficient \(D\) in \([\text{cm}^2 \text{s}^{-1}]\) for the reacting species for a redox reaction is related to the peak current density, \(i_p\), expressed in \([\text{A cm}^{-2}]\), concentration of redox species \(C\) in \([\text{mol cm}^{-3}]\) and scan rate \(v\) in \([\text{V s}^{-1}]\) according to the Randles-Sevcik equation show below:

\[
i_p = 0.4463 n F C \left( \frac{n F D v}{R T} \right)^{1/2}
\]

(7)

Upon plotting the cathodic peak current for copper electrodeposition from Cu\(^{2+}\) ions at 293 K and 1 atm i.e., room temperature and pressure (RTP) and at 423 K and 50 bar i.e., high temperature and pressure (HTP) at as a function of the square root of the scan rate it can be observed that a linear relationship between the two is observed for both cases, as shown in Figure 4-10. Therefore, upon applying the Randles-Sevcik equation the diffusion coefficient for Cu\(^{2+}\) ions in 0.1 M H\(_2\)SO\(_4\) solution is found to be \(1.5 \times 10^{-7}\) cm\(^2\) s\(^{-1}\) and \(7.7 \times 10^{-5}\) cm\(^2\) s\(^{-1}\), respectively. The observed value for the diffusion coefficients are close to the values reported in the literature. In addition to finding that the high temperatures increase the diffusion coefficient of the redox species by 530 times, it is interesting to note that the diffusion coefficient at ETP is close to the values for Cu\(^{2+}\) ions in solution. Upon repeating the study for the effect of scan rate on the peak current, on the microelectrode we obtain a diffusion coefficient of \(8.2 \times 10^{-7}\) cm\(^2\) s\(^{-1}\). As expected the diffusion coefficient obtained from the microelectrode is slightly higher but very close to the values obtained on the macroelectrode.
Figure 4-10. Peak current versus scan rate was used to estimate the effect of ETP on the diffusion coefficient of Cu²⁺ ions on 1 mm diameter GC at RTP (293 K and 1 atm) and HTP (423 K and 50 bar). Pt was used as pseudo-reference electrode.

Effect of temperature and pressure on the deposition mechanism and morphology: Figure 4-11 indicates the results from chronoamperometric studies on carbon substrates from a solution of 10 mM CuSO₄ + 100 mM H₂SO₄. Figure 4-11A illustrates the comparison of the current-time behaviour of electrodeposition carried out at various potentials at RTP with electrodeposition carried out at high temperature and pressure HTP. It is observed that at the every deposition potential, the ones performed at higher temperature and pressure shows higher deposition currents as expected from CV studies. It is also observed that the deposition currents reach steady state very quickly for deposition carried out at both conditions. From figure 4-11B shows the nucleation model curves calculated using the equations developed by Sharifker and Hills. From the figure it is clear that the deposits at RTP were close to instantaneous nucleation as observed previously. However, the Cu deposits at HTP deviate from both instantaneous nucleation and progressive models drastically.

X-ray diffraction was used to identify the effect of temperature and pressure on the crystal structure of the deposition. The diffractograms were analyzed using Xpert Highscore from PAN Analytical.
Figure 4-12 shows the X-ray diffractogram for the electrodeposits obtained on SS316L substrates at -0.8 V vs Pt pseudo reference electrode. Deposits from RTP showed characteristic peaks corresponding to Cu at 43.4°, 50.5°, and 74.2° (JCPDS No. 01-071-4610), and Fe at 44.5° and 65° (JCPDS No. 01-085-1410). However, the deposits obtained at HTP exhibited additional peaks at 36°, a broader, sharper peak at 43° and 74°, and a slight bump at 62° that indicates the possibility Cu2O being present. However, to confirm the presence of Cu2O a technique such as XPS could be used to detect the Cu-O bonds.

![X-ray diffractogram for copper electrodeposited on stainless steel substrates from a solution containing 0.01 M CuSO4 and 0.1 M H2SO4 at 293 K and 1 atm at 423 K and 50 bar. Electrodeposition was performed at -0.8 V vs Pt pseudo-reference electrode, Pt foil was used as the counter electrode.](image)

Figure 4-13A through 4-13C, illustrates the morphology of the copper deposits at 298 K and 1 atm, 423 K and 50 bar. It can be observed that, at room temperature and pressure, the deposits are crystalline and scattered. Although the deposits at 50 bar are crystalline they are closely packed, indicating a higher concentration of Cu2+ ions at the electrode surface due to the high pressure. On the other hand, the electrodeposits at high temperatures indicates a lava type uniformly dispersed layered coating with pores. The pores could be a result of loss of copper due to the comproportionation reaction. The layered type deposit is desired for Cu deposition in trough’s and via’s in the order of 1 um or less, by the semiconductor industry. Levelling agents and accelerator additives have been used predominantly to achieve the formation of Cu+ ions which has been attributed to the formation of uniform conformal coatings. The SEM images from this study has shown that the conformal coatings can be achieved by deposition at higher temperatures and without the complications of additives in the plating baths.
Figure 4-13. SEM images for copper electrodeposited on vitreous carbon substrates from a solution containing 10 mM CuSO₄ and 10 mM H₂SO₄ (A) at 293 K and 1 atm (B) at 293 K and 50 bar, and (C) at 423 K and 50 bar.
4.3 COPPER RECOVERY STUDIES

Chronoamperometry was used to understand the effect of temperature, pressure on the yield, recovery rate, the energy required and the efficiency of copper electrodeposition. An one factor at a time (OFAT) approach was adopted to evaluate the effect of each of the parameter independent of other parameters. Interference effects were not analysed. Also analysed were the effect of the deposition potential, initial copper concentration, and deposition time. The experimental conditions for the various tests are shown in Table 7. Sample chronoamperograms are shown in Figure 4-14 and Figure 4-15.

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<tr>
<th>Expt Label</th>
<th>E (mV) vs mPt</th>
<th>Temp (K)</th>
<th>Pressure (bar)</th>
<th>Cu conc (mM)</th>
<th>Time (min)</th>
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Table 7. Experimental conditions for the OFAT study, that was employed to understand the effect of the temperature and pressure on the recovery of copper.

![Figure 4-14](https://example.com/figure-4-14.png)

Figure 4-14. Chronoamperometry results for copper recovery with a constant potential of 700 mV vs mPt at 298 K and 1 bar from a solution containing an initial copper concentration of 10 mM at pH of 1.
Figure 4-14 illustrates the current density and charge as a function of time obtained from chronoamperometry experiments performed at a potential of 700 mV vs mPt at a temperature of 298 K and pressure of 1 bar. The plot in figure is divided into 3 regions, the region 1 at the start of the experiment shows plot beginning at a high negative current with a sudden drop in the magnitude of the current. This region corresponds to the instant nucleation at highly active sites on the substrate. Upon loss of active sites, further deposition takes place by growth on the nucleated sites shown by the increase in the current in region 2. Upon further deposition, the concentration of the Cu^{2+} ions in the bulk decreases resulting in a drop in the magnitude of the deposition current, which is marked by region 3 and is referred to the concentration polarization region. Maximum efficiency is obtained by maintaining the deposition in the growth phase of the deposition.

Figure 4-15. Results from chronoamperometry measurements performed at 423 K and 50 bar illustrating (A) Effect of electrodeposition potential vs mPt with a solution containing an initial copper concentration of 10 mM and (B) Effect of initial Cu concentration on the copper electrodeposition performed at 600 mV.

From Figures 4-15A, it can be observed that the copper deposition current densities at elevated temperature and elevated pressure are higher at potentials -600 mV and -700 mV, implying (1) rapid deposition and (2) current density contributions from secondary reactions. It is also noted that there are more than one nucleation-growth-concentration polarization cycles for electrodeposition carried out at potentials of 600 mV, 700 mV. The successive nucleation-growth-concentration polarization cycles can be attributed to the replenishing of Cu^{2+} concentration at the electrode surface from disproportionation of Cu^{+}, which in-turn formed from the comproportionation of metallic Cu and Cu^{2+} ions as shown in Equation 1. The increased temperatures tends to shift the equilibrium of equation 1 to the right.

\[
\text{Comproportionation / Disproportionation} \quad \quad Cu^{2+}_{\text{aq}} + Cu \rightleftharpoons 2 Cu^{+}_{\text{aq}} \quad \quad K_{eq} = 6 \times 10^{-7} \text{ M} \quad (1)
\]

Figure 4-15B shows that the copper deposition current densities at -600 mV, corresponding to initial copper concentrations of 10 mM and 5 mM shows that the deposition with a higher copper concentration showed higher deposition current densities, while both concentrations exhibited a second nucleation-growth cycle towards the end of the deposition period. On the other hand, the current densities for copper deposition from an initial Cu^{2+} concentration of 2.5 mM, shows a steady current possibly indicating that the electrodeposition and the comproportionation reactions are in equilibrium.

Figure 4-16, illustrates the effect of initial copper concentration, deposition potential, and deposition time at ETEP (423 K and 50 bar) on the faradaic efficiency, yield, rate of recovery, and energy required for an unit mass of copper. The efficiency of electrodeposition was calculated based formula listed in Equation 2:
Efficiency (%) = \frac{\text{Experimental mass of Cu electrodeposited}}{\text{Theoretical mass of Cu deposited}} \times 100 \quad (2)

\text{Theoretical mass of Cu deposited} = \frac{M(R)}{2F} \quad (3)

where, M is the molecular weight of copper (63.55 mg mol\(^{-1}\)), \(R\) is the experimental charge passed in coulombs, \(z\) is electrons required to deposit one mole of the metal, and \(F\) is the Faraday’s constant (96485 C). Yield is the ratio of metal recovered to the amount of metal initially present in the solution given by Equation 4, whereas the rate of recovery is defined as the amount of metal deposited to the duration of the experiment expressed in mg hr\(^{-1}\) and the energy required for recovering a unit mass of the metal is given by Equation 5.

Yield (%) = \frac{\text{Experimental mass of Cu deposited}}{\text{Mass of Cu ions in the solution}} \times 100 \quad (4)

\text{Energy Required (Wh g}^{-1}) = \frac{\text{Electrodeposition Potential (V)} \times \text{It}}{\text{Experimental mass of Cu deposited (g)}} \quad (5)

![Figure 4-16. Effect of (A) initial copper concentration (B) copper electrodeposition potential vs mesoporous Pt reference (mPt) electrode, and (C) time on the Faradaic efficiency of Cu recovery (%), yield, recovery rate in mg hr\(^{-1}\) and energy required for Cu recovery in Wh g\(^{-1}\) at 423 K and 50 bar. The energy required is pre-multiplied by 10 in order to make differences visible in the chosen scale. To obtain the actual energy required in Wh g\(^{-1}\) divide by 10. Unless specified the recovery was carried out in a solution of 10 mM CuSO\(_4\) and 100 mM H\(_2\)SO\(_4\) at 700 mV vs mPt for 60 minutes. The error bars were obtained by propagation of errors in individual ICP readings.](image)

Figure 4-16A illustrates the effect of initial Cu concentration on its recovery after 1 hr at 423 K and 50 bar. It is observed that although a slight increase in deposition efficiency, there is no significant difference in the range of initial copper concentration evaluated. On the other hand, the recovery rate for the solution with 10 mM Cu\(^{2+}\) was significantly higher than the recovery from 5mM Cu\(^{2+}\) solution, which can be attributed to the higher deposition currents, which is directly proportional
to the concentration of the ionic species of interest in the solution. The recovery study with higher copper ion concentration showed higher reduction currents as shown in Figure 3B. As expected, the variation in the energy required for recovery is follows a trend that is opposite to the efficiency of the recovery and that the solution with the least initial concentration required the highest energy for recovery.

Figure 4-16B, illustrates the effect of the deposition potential on the efficiency, yield, and recovery rate of Cu from 10 mM Cu solution, at 423 K and 50 bar. A clear improvement in the deposition efficiency is achieved at -575 V vs mPt, on the other hand no significant advantage is observed for any of the deposition potential over another. This could be attributed to the fact that upon deposition of copper the surface potential at -600 mV and -700 mV vs mPt was sufficient enough partially direct some of the currents towards hydrogen evolution reaction, thereby reducing the efficiency of electrodeposition.

Figure 4-16C, shows the effect of deposition time for recovery from a solution containing 10 mM Cu²⁺ solution at 600 mV, at 423 K and 50 bar. As for the duration of the experiment, it can be observed that the maximum yield, maximum recovery rate, as well as maximum efficiency was achieved at 33 minutes. Despite, 20% of the copper ions still remaining undeposited and in solution, the drop in efficiency this could be attributed to the depletion of Cu²⁺ ions from the solution as they are deposited.

Figure 4-17, shows the effect of temperature and pressure on the Faradaic efficiency, yield, rate of recovery, and energy required for Cu recovery. From the figure it is clear that the lowest efficiency and the highest energy required for copper recovery at 298 K and 1 bar. No significant difference was found for the efficiency, yield, recovery rate, and energy required for electrodeposition at 298 K and 50 bar higher and the electrodeposition at 423 K and 50 bar. Despite the higher diffusion coefficients and higher kinetics rate of deposition expected from Arrhenius equations, the improved efficiencies, yields, recovery rates, and energy required for recovery are clearly absent from the data observed. This can be attributed to the possible loss of Cu from the surface due to the comproportionation reaction as shown in the Equation 1.

In order to determine the loss of Cu from the surface due to the comproportionation / disproportionation reaction, a Cu sheet of known area and mass was exposed to a stationary CuSO₄ solution in 100 mM H₂SO₄ at various conditions shown in Table 2. Cu samples were treated in a concentrated solution of HNO₃ to remove any impurities present on the surface by oxidizing them, followed by washing them in deionized water, rinsing them in ethanol and water. The samples were
then dried and weighed before exposure to the experimental conditions. The mass of Cu before and after exposure was weighed, to estimate the loss of Cu from the sample. Each experiment is repeated twice and the average mass lost along with the standard deviation is shown in Figure 6.

Figure 4-18. Effect of (A) temperature (B) pressure, (C) Cu
ion concentration in solution, (D) sample surface area, and (E) time on the rate of Cu loss from the sample. Unless specified the recovery was carried out in a solution of 10 mM CuSO₄ and 100 mM H₂SO₄ for 60 minutes. The error bars were obtained from the standard deviation of two repeated measurements.

From Figure 4-18A, as the temperature increases from 298 K to 423 K, a significant increase in the rate of Cu loss from the sample is observed, indicating a significant increase in the rate of the comproportionate reaction. This increase in the rate can be derived from Vant-Hoff equation and has been confirmed in a rotating disk electrode study at temperatures up to 353 K. It is observed Figure 4-18B that, as the pressure increased from 1 bar to 50 bar, the rate of the loss of Cu from the sample decreased by a factor of ~30 implying a retardation of the comproportionate reaction. Figure 4-18C shows that the change in the rate of Cu loss from the sample is a quadratic function of the concentration of Cu²⁺ ions in the solution. As expected for a heterogeneous reaction, Figure 4-18D indicates that at 423 K and 50 bar, the rate of the reaction varies directly as a function of the area.
of the sample. Finally, it can be observed that the rate of Cu loss and hence the rate of the comproportionation reaction increases logarithmically as a function of time. Although, from Figure 4-19, one can expect the area to increase exponentially, the amount of Cu$^+$ in the solution increases, thus tending to reach equilibrium in turn resulting in a logarithmic increase in the rate of Cu loss, as opposed to an exponential rate of Cu loss.

Figure 4-19. SEM images of Cu sheet samples (A) before and (B) after exposure for 1 hour in a solution of 10 mM CuSO$_4$ and 100 mM H$_2$SO$_4$ at 423 K and 50 bar.
5 Conclusions

Mesoporous platinum deposits on a Pt disk, with pore size ranging between 5 nm and 10 nm, was achieved on Pt. The electrodes showed a rapid and stable potential response. Additionally, the stability of the electrode with temperature was confirmed. The mPt quasi-reference electrode was calibrated with the help of Fe(II)/Fe(III) redox couple. The equilibrium potential of the mPt electrode was found to vary linearly with temperature according to the expression:

\[ E_{\text{mPt}}(\text{vs SHE}) = 0.6108 - 2.5 \times 10^{-3}(T - 298) \]

where, \( E_{\text{mPt}} \) is the equilibrium potential of the mPt quasi-reference electrode expressed in V vs SHE, and \( T \) is the temperature in K.

Cyclic voltammograms indicate that the electroreduction of \( \text{Cu}^{2+} \) ions and subsequent electrooxidation of \( \text{Cu} \) in aqueous medium at elevated pressures exhibit no significant difference when compared to that at atmospheric pressure. However, SEM images indicate that the electrodeposits at elevated pressures are more dense and closely packed. As expected, at temperatures greater than the 373 K and elevated pressures, the cyclic voltammograms exhibited currents that were at least 10 times higher than that obtained at room temperatures. Additionally, the deposit morphology at 373 K does not exhibit a crystalline-type deposit as observed at room temperature, and showed layered deposit which was rather scattered and porous. The porous nature of this deposit can be attributed to the Cu dissolution due to the increased rate of comproportionation reaction at higher temperatures, resulting in the formation of \( \text{Cu}^+ \) ions, which has been shown to be a primary reason behind a uniform conformal coating.

A one factor at a time (OFAT) study was performed to understand the independent impact of temperature, pressure, initial copper concentration, deposition times, and electrodeposition potential on the Faradaic efficiency, yield, recovery rate, and energy required to recover copper was performed. From the study, it can be concluded that the maximum efficiency and minimum energy required to was obtained for both solutions at elevated pressure and solutions at ETEP, indicating that it could be a potential technology that can be used for metal recovery from geothermal fluids. A factorial design or an optimal design of experiments for the major parameters is essential to understand the interaction synergistic or opposing effects of the parameters on the recovery of copper.
6 References


